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THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON
BINDER FOR HIGH ENERGY SOLID PROPELLANTS

by

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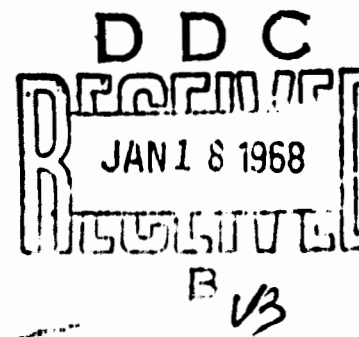
Quarterly Technical Report AFRPL-TR-68-9

January 1968

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FOREWORD

This technical report was prepared under Contract No. AF 04(611)-11419 as partial fulfillment of the requirements of Project 3418 of the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California. The work reported was done in the Chemical and Physical Sciences Department of the Aerojet-General Corporation, Sacramento, California. This report was designated Aerojet-General Corporation Report 1030-82Q-7 and covers the results of work done during the interval 14 September to 13 December 1967. The project was a follow-on to the project completed under Contract AF 04(611)-10386, the results of which are reported in AFRPL-TR-67-158. This document reports on Phases Four and Five. This project was monitored by Mr. Robert Corley.

Acknowledgment is made to the following persons who have contributed materially to the work performed during this period: A. J. Hammond, Senior Chemist, J. L. Humphreys and T. F. Manning, Chemists, F. H. Davidson, Liaison Engineer, Mechanical Properties Laboratories; and at The General Tire and Rubber Company to R. G. Chase, Technical Assistant to the Technical Coordinator, Research and Development. Special acknowledgment is made to Mr. C. Gustavson, who is no longer a member of this group, but who contributed significantly to the work reported here.

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Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

Work was continued on the study of Telagen S prepolymers for conventional and advanced propellant systems. The factors affecting low temperature behavior of conventional systems and a replacement for CTI received most attention this quarter. Saturation of Telagen prepolymers definitely causes poor low temperature properties in binders and propellants. This was established by studies with a series of related polymers differing only in saturation. Mixtures of saturated and unsaturated prepolymers were not as good as a partially saturated prepolymer for low temperature behavior. Prepolymer molecular weight and the nature of the crosslinker had very little effect on the low temperature mechanical properties. Telagen S prepolymers have been characterized by chromatography on silica gel. The Esso technique has been simplified and an infrared method was used to follow the functionality of the eluted polymer. Preparative chromatography to obtain difunctional prepolymer for binder and propellant studies was developed. Aging studies were continued and aging of binders with partially saturated prepolymers was begun.

The study of advanced systems was continued by model compound and propellant investigations using HDP and HAP. Acetylazetidine and 2,5-dioxaspiro[3,3]heptane were incompatible with HAP and only the latter was compatible with HDP. However the dioxaspiroheptane did not react with acid at 50°C. It was observed that HAP and HDP very rapidly dehydrate secondary alcohols. With these materials only primary alcohols may be used. Some HAP propellants were made.

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AFRPL-TR-68-9

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GLOSSARY

C_1 and C_2	Mooney-Rivlin Constants
C-1	N,N-di-(2-cyanoethyl)-2,3-dihydroxypropylamine
Carwinate M-125	4,4'-Diisocyanatodiphenylmethane, product of the Upjohn Company
CTI	Diisocyanate, proprietary item of the Aerojet-General Corporation
DDI 1410	Dimeric diisocyanate derived from Emery Dimer Acid, product of General Mills, Inc.
E_0	Initial uniaxial modulus
E-246	Multifunctional isocyanate, product of Mobay Chemical Company
FeAA	Ferric acetylacetonate
GLC	Gas-liquid chromatography
GTR	Glycerol triricinoleate
HAA	Acetylacetone
HDI	Hexamethylene diisocyanate
IDP	Isodecyl pelargonate, product of Emery Industries, Inc.
meq/gm	Milliequivalents per gram
mm/gm	Millimoles per gram
NMR	Nuclear magnetic resonance
Oronite 6	Liquid polyisobutylene, product of the California Chemical Company
PAPI	Polyphenyl polyisocyanate, product of the CPR Division, Upjohn Company

GLOSSARY (cont)

Polycin 23	Diol, product of Baker Castor Oil Company
Polycin 51	Diol, product of Baker Castor Oil Company
Telagen	Functionally-terminated polybutadiene, product of The General Tire and Rubber Company
Telagen S	Functionally-terminated hydrogenated polybutadiene, product of the General Tire & Rubber Company
$\text{TiO}(\text{AA})_2$	Titanyl acetylacetonate
TMP	Trimethylolpropane
VPO	Vapor phase osmometer
ϵ_b	Uniaxial strain at break
ϵ_m	Maximum uniaxial strain
σ_b	Uniaxial break stress
σ_m	Uniaxial maximum stress

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THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER
FOR HIGH ENERGY SOLID PROPELLANTS

I. INTRODUCTION

This is the seventh Quarterly Technical Report submitted in partial fulfillment of the requirements of Contract AF 04(611)-11419. The report covers the period 14 September through 13 December 1967.

II. OBJECTIVE

The objective of this program is to further develop and evaluate a solid propellant binder system specifically to meet the most rigid demands of advanced, high performance solid rocket motors. The solid propellant binder system consists of an isocyanate-cured, saturated hydrocarbon prepolymer developed and evaluated under Contract AF 04(611)-10386. Further development and evaluation will involve propellant optimization, testing of curatives for room temperature cures, replacing CTI, attaining better low temperature properties, determining the effect of burning rate modifiers, adaptation to advanced fuels and oxidizers, formulations containing both advanced fuels and oxidizers, and a study of environmental stability.

III. SUMMARY

A. A series of three prepolymers made from the same polybutadiene were obtained from The General Tire and Rubber Company. These prepolymers were from 0 to 93% saturated. They were characterized and the results are reported.

B. A pilot plant batch of CTI was made. The yield was 55% of material with an equivalent weight of 72.3 (theoretical, 69.0). The isocyanate, Carwinate 125M was purified by crystallization of a hexane soluble fraction. This purification technique did not succeed with Mobay E-246.

C. Small and large scale chromatographic fractionations of Telagen S have been made. The technique is a simplified variation of that developed by workers at the Esso Research & Engineering Company and involves the use of three solvents for small scale characterization studies and a single solvent for large scale preparative studies. The characterization studies have been in general agreement with the Esso work. The preparative work is designed to isolate difunctional material for preparation of propellant.

D. A novel method for following functionality changes during chromatography of Telagen S was developed. The functionality of the eluted polymer is estimated from the ratios of the intensities of the OH band at 3330 cm^{-1} to CH bands at 1380 and 1460 cm^{-1} .

E. The effect of saturation on the low temperature behavior of Telagen S binders has been determined from a series of related prepolymers. The results confirm the previous conclusion that saturation is the single most pronounced effect tending to give poor low temperature behavior. While the use of mixtures of a saturated and an unsaturated prepolymer gives some improvement of low temperature mechanical properties, the mixture is not as effective as a partially saturated prepolymer of equivalent olefin content.

F. The mechanical properties at low temperature differ very little for binders made with unsaturated and 60% saturated prepolymer. The low temperature behavior changes radically at saturations between 60 and 90%. The effect of prepolymer molecular weight is very slight. No effect of crosslinkers on low temperature properties was observed for binders crosslinked with GTRO, E-246, and PAPI.

G. Generally the conclusions regarding the effects of saturation, prepolymer molecular weight, and crosslinkers have been substantiated by propellant studies.

H. GTRO, Mobay E-246, and PAPI were studied as replacements for CTI and all are considered good prospects. Binders crosslinked with GTRO give properties which are not highly dependent upon the crosslink densities.

I. Actylazetidine was incompatible with HAP. The azetidine was consumed with no loss of the co-reactant, propionic acid. The oxetane, 2,5-diospiro[3,3]heptane, was compatible with HDP but not with HAP. The oxetane and acid did not react at 50°C .

J. The reactions of 1-octanol and of 2-ethylhexanol with n-1-decenylsuccinic anhydride were too rapid and the method used could not determine which alcohol reacts faster. Similarly the rates of n-1-decenylsuccinic and dodecylsuccinic anhydrides with 1-octanol could not be distinguished by the method used because the rates were too rapid.

K. Model compound studies of HDP or HAP propellants show that secondary hydroxy terminated alcohols, in stirred or mixed composites, were dehydrated very rapidly (faster than about $8\%/min.$). The dehydration rate was markedly higher with HDP.

L. Advanced propellant studies with primary hydroxy terminated prepolymers indicated that Oronite 6 is better than IDP as plasticizer and that GTRO is better than TMP as crosslinker. A cure catalyst is not required.

M. Aging studies on binders made with prepolymers of different saturation have begun. No data are available.

IV. TECHNICAL DISCUSSION

A. TASK ONE

1. Introduction

Task One involves prepolymer characterization, improved low temperature properties, curing agent substitutes for CTI, the effects of plasticizer and burning rate modifiers, room temperature curing and boron-workhorse binder systems. A propellant designed for low temperature capability, a propellant cured at room temperature, and a propellant with a CTI replacement will be prepared for long-term aging.

2. New Prepolymers

The General Tire and Rubber Company has submitted an unsaturated prepolymer and two partially saturated ones derived from it. The prepolymers and some of their properties are listed in Table I.

Table I

PROPERTIES OF SOME TELAGEN S PREPOLYMERS

Lot No.	242AM-169	3HPL-123	3HPL-125
Molecular Weight (VPO)	1600	-	-
Equivalent Weight	1080	1130	1150
Hydroxyl Content, meq/gm	0.928	0.883	0.872
Unsaturation, mm/gm	17	6	1
1,2-vinyl, %	34	6.8	0
1,4-trans, %	28	-	-
1,4-cis, %	38	-	-
Brookfield Viscosity, poises at 25°C	36	95	325

3. Characterization of Ingredients

a. New Prepolymers

The degree of saturation of prepolymers recently received from The General Tire and Rubber Company was determined by combination of NMR to determine total protons on olefinic groups and IR to determine total vinyl groups. The results, assuming the unhydrogenated polybutadiene to be 100% unsaturated, are: 242AM-169, 100% unsaturated; 3HPL-123, 39.6% unsaturated; 3HPL-125, 7.2% unsaturated. The corresponding values determined by The General Tire and Rubber Company are 100, 35.3, and 5.9%; agreement is satisfactory for the intended experiments.

b. CTI

A large batch of CTI was made in pilot plant equipment with a 55% yield based on 15 lb of starting material. The equivalent weight of the product was 72.3 (theoretical, 69.0). An earlier batch in pilot plant equipment had given a very low yield. The present run demonstrates the successful scale up of CTI preparation.

c. Carwinate 125M

Impure Carwinate 125M (4,4'-Diisocyanatodiphenylmethane), equivalent weight of 145, was refluxed with hexane. The yellow crystals, which separated, from the cooled hexane, had a melting point 30-31°C and an equivalent weight of 126 (theoretical 125).

d. Mobay E-246

Mobay E-246, a multifunctional aromatic isocyanate (functionality, 2.69), is a dark liquid. The successful purification of the Carwinate 125M encouraged an attempt to purify E-246. The purification was not successful.

E-246 is very soluble in benzene, toluene, dichloromethane, chloroform, and carbon tetrachloride, is moderately soluble in cyclohexane, and very slightly soluble in hexane, heptane, and p-xylene. The E-246 was extracted with cyclohexane and with hexane, but in both cases the infrared spectrum of the soluble portion was similar to that of the original. There was no difference in the equivalent weights determined by the dibutylamine method.

e. Functionality of DDI-1410 and GTRO

VPO molecular weight studies of DDI-1410 and GTRO used in experiments described in this report were made. The molecular weight of DDI-1410 was 608. Its functionality was 2.06 based on an experimentally determined equivalent weight of 295. The GTRO had a molecular

weight of 903 (theoretical molecular weight of 932) and an equivalent weight of 342 which corresponds to a functionality of 2.64.

4. Chromatographic Studies

a. Experimental

The successful fractionation of Prepolymer 148AH into non-, mono-, and difunctional components by workers at the Esso Research and Engineering Company⁽¹⁾ encouraged further experiment along these lines. The complex solvent system used by these workers was simplified and applied to several prepolymers, the objective being to determine the non- and mono-functional contents of the prepolymers.

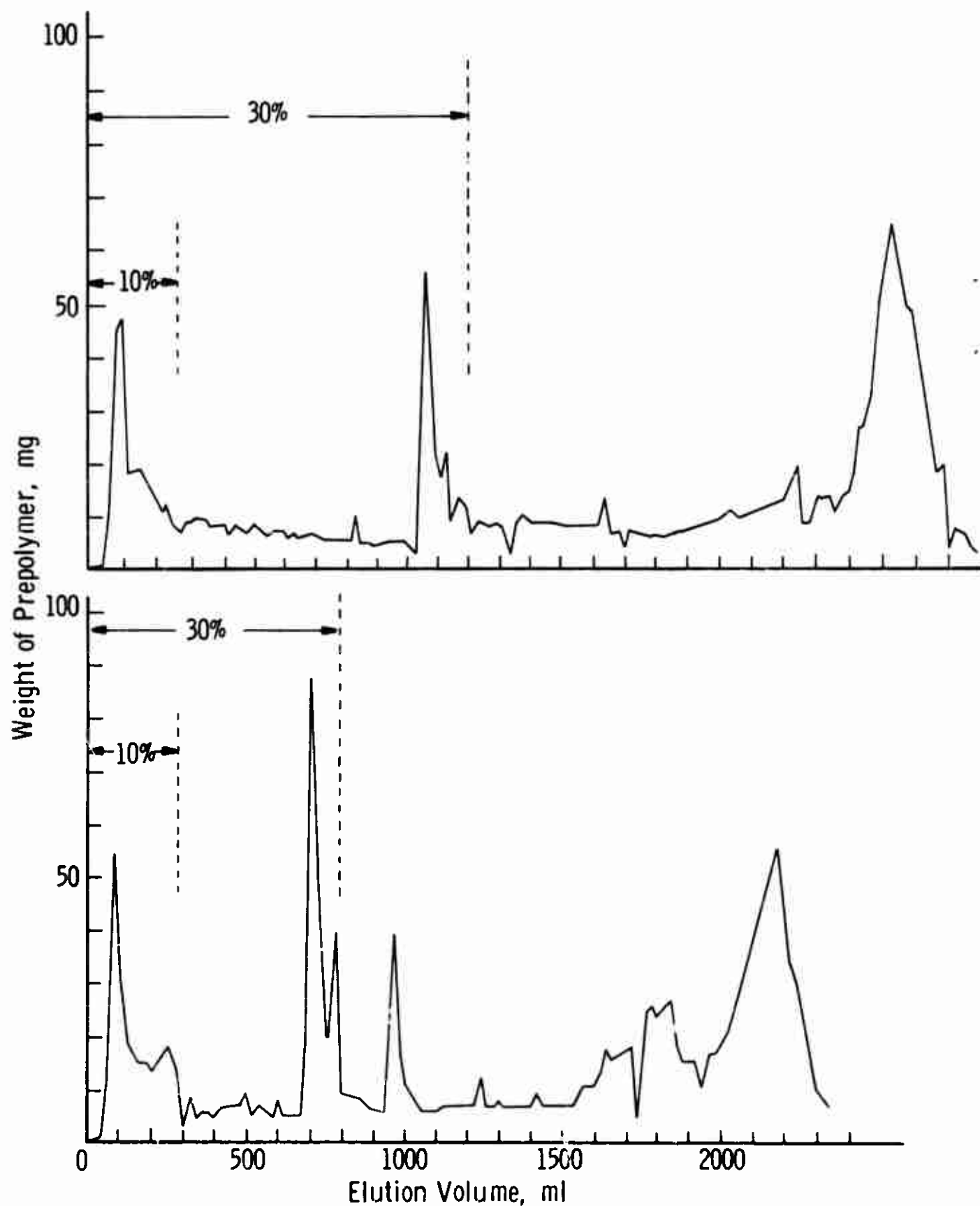
Two grams of 148AH were introduced into a 7/8" diameter column packed with 100g of 100-200 mesh silica gel in CCl_4 . CCl_4 , CHCl_3 , and CH_2Cl_2 (1200 ml of each) were used to elute the material from the column and 20-ml fractions were collected by an automatic fraction collector. The solvent was evaporated and an elution profile constructed. The results, similar to those reported by Esso, showed three distinctly separate major fractions. About 30% of the material is non-functional and monofunctional. A duplicate run was made to check these results. While the duplicate showed some differences with respect to retention times, the fractions and their quantities were similar to those obtained in the first experiment. The elution profiles are illustrated in Figure 1.

An infrared spectrum of each of the three major fractions was run in a semi-quantitative method to determine their functional group content. The first fraction (approximately 10% of the total) showed very low OH absorption and the second fraction (approximately 20% of the total) showed a higher OH absorption which, however, was lower than that of the third fraction.

The above procedure was also applied to fractionate prepolymers 158H and 161AHR. The results with 161AHR were almost identical to those with 158H except for the percentage of material comprising each of the three major fractions. With 161AHR, the first fraction contained approximately 13% of the total material, and the second fraction contained an additional 17%.

(1) B. E. Hudson and A. H. Muenker, "Functionality Determination of Binder Prepolymers", Esso Research and Engineering Company, Quarterly Progress Report 3, GR-3-FBP-67, 1 April to 30 June 1967. Contract No. FC46111-67-C-0012.

CHROMATOGRAPHIC FRACTIONATION OF PREPOLYMER 148AH
ON SiO_2



The results of both 158H and 161AHR compare very closely with those found for 148AH. The elution profiles are shown in Figure 2 and the data are summarized in Table II. The size of Fraction III did not correlate with the functionality derived from curing studies. Thus the functionality of Prepolymer 148AH was judged to be higher than that of 158H or 161AHR which were approximately similar. The calculated functionalities of these prepolymers, eliminating the nonfunctional Fraction I and assuming non-recovered material as part of difunctional Fraction III, are: 148AH, 1.78; 158H, 1.82; and 161AHR, 1.80.

Table II

FRACTIONATION OF TELAGEN S

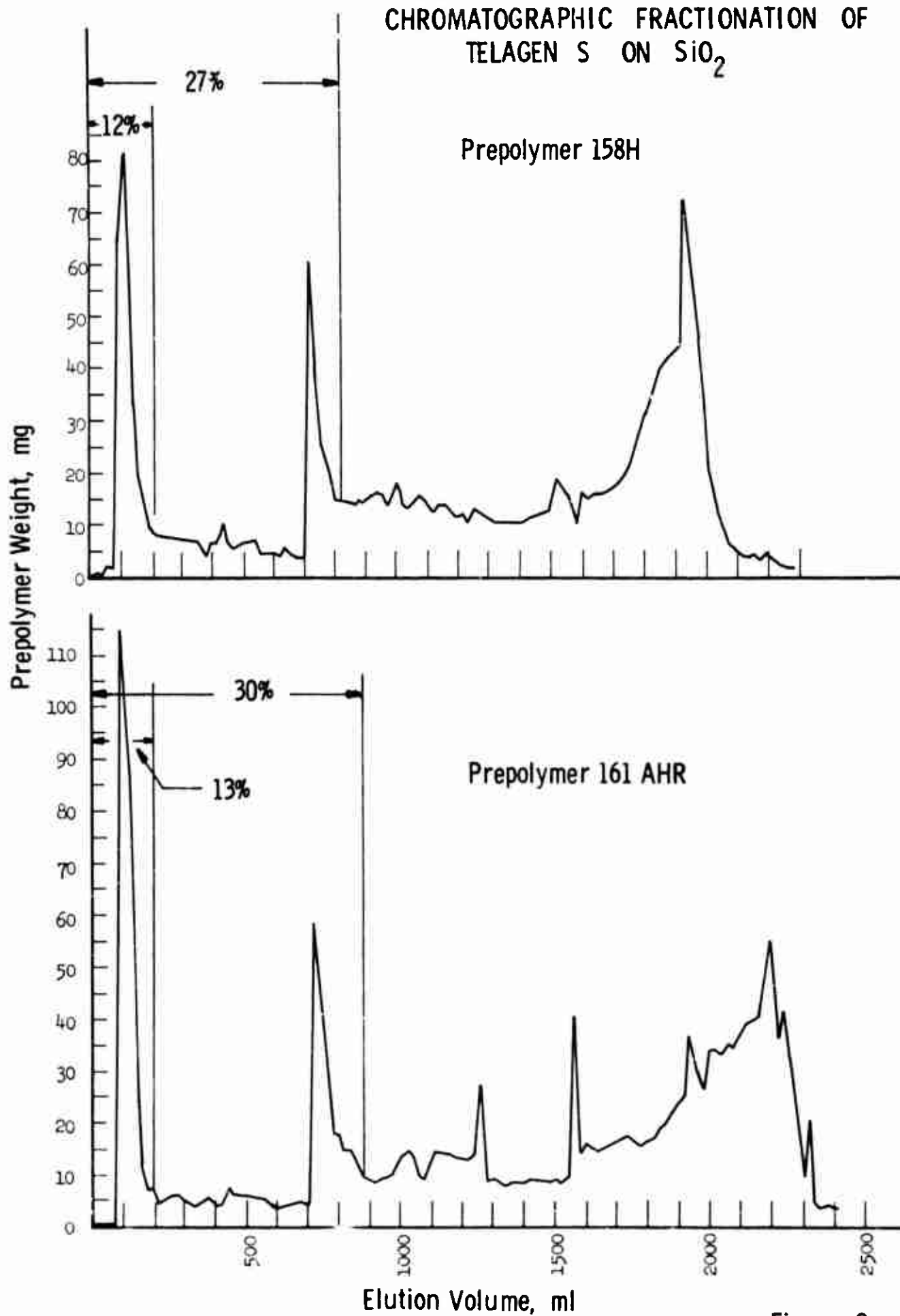
Prepolymer Lot No.	Composition, wt% of original Fraction		
	I	II	III ^a
148AH	10	20	70
158H	12	15	73
161AHR	13	17	70

^aMaterial not recovered from the column (about 10% for 148AH and 158H) included.

b. Preparative

An effort was made to separate enough of the difunctional Fraction III to prepare propellants. The column used was four feet in length and three inches in diameter. Five pounds of silica gel (100-200 mesh) were slurried with chloroform and placed in the column giving a three foot bed. Fifty grams of Prepolymer 158H were diluted to 50% with chloroform and added to the column. The progress of the elution was followed by infrared spectroscopy. The intensity of the CH band at 2940 cm^{-1} showed the amount of prepolymer passing through the column. The non- and monofunctional prepolymers were eluted after sixteen fractions, each 500 ml of CHCl_3 collected at 1 liter per hour. Fractions 1 to 11, after evaporation of the solvent, showed no OH band at 3330 cm^{-1} , but Fractions 12 to 16 showed OH absorption.

CHROMATOGRAPHIC FRACTIONATION OF
TELAGEN S ON SiO_2



The functionalities of the fractions were determined from the ratios of intensities of the hydroxyl band (3330 cm^{-1}) to those of the CH bands at 1460 cm^{-1} and 1380 cm^{-1} . Prepolymer 158H (functionality, 1.68) was the standard from which the relative intensities to be expected for a given functionality of the fractions were determined (Table III).

Table III

RELATION OF RELATIVE INTENSITIES OF INFRARED BANDS
TO MONO- AND DI- FUNCTIONALITY FOR PREPOLYMER 158H

<u>Functionality</u>	<u>Expected Relative Intensities</u>	
	<u>3330/1460</u>	<u>3330/1380</u>
1	0.212	0.446
2	0.425	0.892

The CH band at 2940 cm^{-1} could also have been used for this determination, but it is so intense relative to the OH band that two solutions of proper concentration would have been required for the Perkin-Elmer laboratory instrument used for this study.

Table IV indicates the results and the infrared spectrum of Fraction 18 which is the difunctional fraction is shown in Figure 3.

Table IV

PREPARATIVE CHROMATOGRAPHY OF PREPOLYMER 158H

<u>Fraction No.</u>	<u>Weight g</u>	<u>Weight Percent</u>	<u>Functionality</u>
1 to 8	4.1	8.2	0
9 to 11	7.9	15.8	0
12 to 14	5.9	11.8	0.75
15 to 16	4.1	8.2	0.99
17 ^a	11.7	23.4	1.14
18 ^b	9.4	18.8	2.55 ^c
Recovery	43.1	86.2	

^aCHCl₃ fraction just preceding acetone flush

^bAcetone-water flush

^cValue on undried sample

INFRARED SPECTRUM OF FRACTIONATED PREPOLYMER 158H
(Arrows show bands used for calculating functionality)

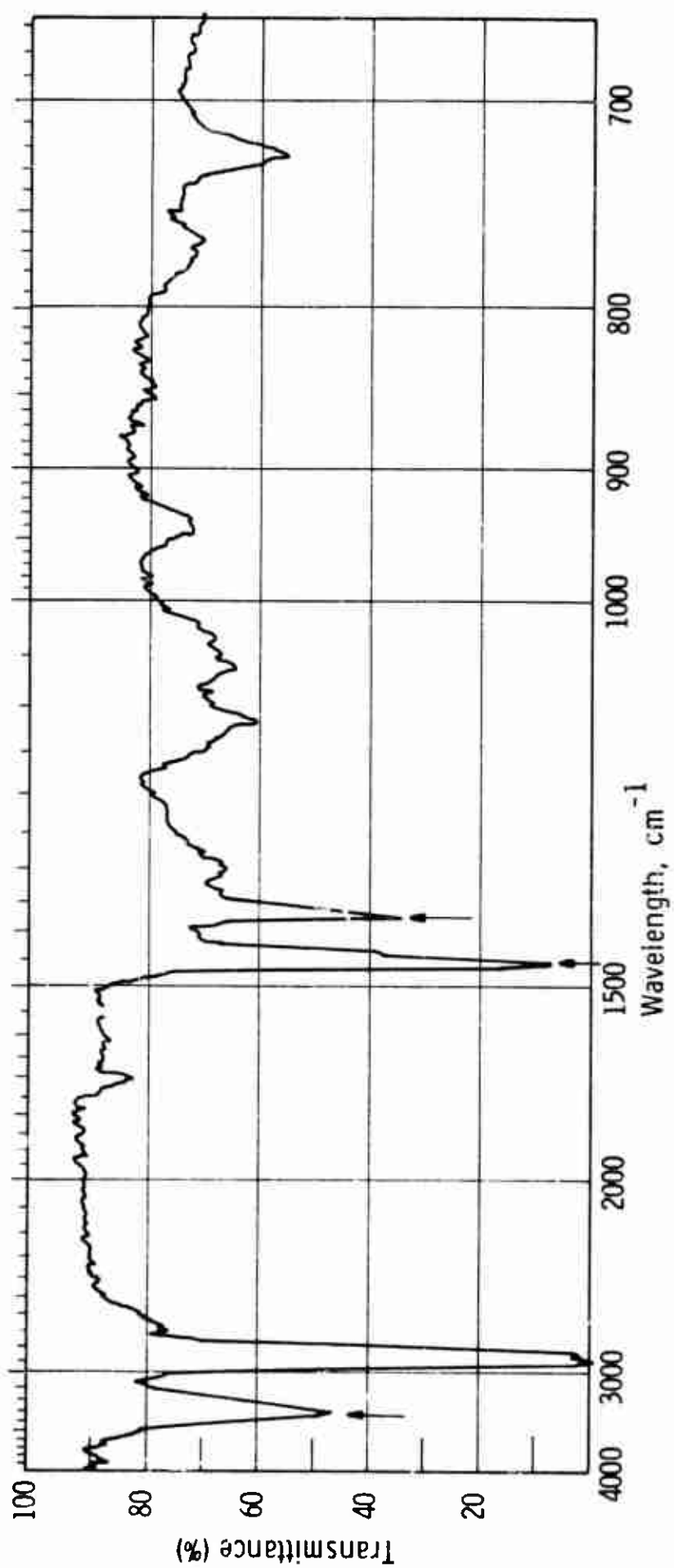


Figure 3

The large scale separations are continuing to obtain 50 to 100g of prepolymer of functionality close to two. Subsequently this material will be used to prepare propellant. The results of the large scale separations do not match exactly those obtained in the smaller scale ones, but the purpose of the large scale work is to separate large quantities (in a relative sense) of material of higher functionality. To achieve this purpose, some fractionation efficiency is sacrificed for speed and quantity.

5. Prepolymer Functionality

The inadequacy of using functionality as determined from the ratio of molecular weight to equivalent weight ratio to formulate propellant binders has been frequently pointed out during this program. A typical example is Prepolymer 168H with a functionality of 1.63 as determined by the molecular weight to equivalent weight ratio. Such a polymer should require an HDI to CTI equivalents ratio of 2.25 for incipient crosslinking. In reality binders with a crosslink density of about 1×10^{-5} moles of chains per cubic centimeter have been made at an HDI to CTI ratio of 6.0. It is not known whether this situation arises from a higher actual functionality of the prepolymer, entanglements formed on curing, or crosslinks introduced by side reactions, but this fact is an experimental reality.

To cope with this situation, the idea of "practical" functionality was introduced. Practical functionality was calculated from a cured binder whose crosslink density was known by the relation

$$X_D = \sum_{i=1}^n \left[(f_i - 2) W_i / E_i f_i \right] \text{ where } X_D = \text{crosslink density in moles of branch}$$

points per gram, f_i = functionality of a binder component, W_i = weight fraction of a binder component, E_i = equivalent weight of a binder component, and the sum taken over all n reacting components (plasticizer is excluded since it is not reacted). The equation has these limitations: it assumes 100% reaction during polymerization and is valid only where the branch point has a functionality of 3. With the isocyanate system the extent of reaction is very high and the branch points can be kept to a functionality of 3.

The crosslink density has been determined from the Mooney-Rivlin C_1 constant, from the gel fraction, from the compression modulus of a swollen binder and from the uniaxial equilibrium modulus of a binder. All of these yield consistent values for the practical functionality from binders with wide range of HDI to CTI ratios. Table V lists the functionalities by the molecular weight to equivalent weight ratio and practical functionalities for a number of prepolymers used in this program.

Table V

PRACTICAL FUNCTIONALITY OF TELAGEN S PREPOLYMERS

<u>Prepolymer</u>	CTI/HDI at ^a <u>X_D=0</u>	<u>No. of Data</u>	<u>Functionality</u>	
			<u>Practical</u>	<u>M.W./E.W.</u>
8507-I-47.1	-0.119	3	2.01	1.71
242AM-148A ^b	-0.014	6	2.00	1.70
242AM-148AH	0.0611	20	1.98	1.62
242AM-158H	0.0136	11	1.92	1.68
242AM-161AHR	0.191	8	1.91	1.49
242AM-168H	0.0662	7	1.96	1.63

^aCTI to HDI equivalents ratio required for incipient crosslinking. A negative value indicates prepolymer can crosslink without a crosslinking agent.

^bUnsaturated precursor of Prepolymer 148AH.

6. Low Temperature Properties

a. Introduction

Work done during the previous quarter (see Report AFRPL-TR-67-260) indicated that the single most important factor influencing the low temperature behavior of saturated binders was the degree of saturation. The work of this quarter continued to confirm and to extend this finding and to apply it to propellant studies. The effect of several curing agents was shown to be negligible as far as low temperature behavior is concerned.

b. Binder Studies

(1) General

The binders prepared and their properties are summarized in Table VI. This table also includes binders made in the

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Table VI

COMPOSITION^a AND PROPERTIES OF TELAGEN S BINDERS

Reference No.	Composition		Mechanical Properties							Ratio of Mech. Prop. at -40° to 77°F	
	Prepolymer Crosslinker	HDI/CTI ^b	Temp Of	σ_m psi	ϵ_m %	ϵ_b %	E_o psi	C_1 Kg/cm ²	C_2 Kg/cm ²	σ	E_o
200	11.8AH/11.8A ^d CTI	3.0	77 -40	9 310 ^e	1480 ^e 1410 ^e	480 -	4 268	0.41 1.96	0.042 1.45	34	67
201	25.7 CTI	3.0	77 -40	3 ^e 175	740 ^e 526	- 528	7 158	0.009 0.48	0.003 1.01	58	23
202	11.8AH/25.7 ^f CTI	3.0	77 -40	22 303 ^e	310 ^e 382 ^e	315 ^e 385 ^e	19 208	0.17 1.38	0.012 0.76	14	11
203	3HPL-96 CTI	4.0	77 -40	15 554 ^e	360 335 ^e	360 339 ^e	11 553	0.075 2.95	0.042 2.10	37	50
204	3HPL-97 CTI	3.5	77 -40	46 785 ^e	500 343 ^e	500 345 ^e	42 1136	0.13 2.60	0.30 9.00	17	27
205	3HPL-96 ^g CTI	2.0	77 -40	79 2500 ^e	214 ^e 117 ^e	214 ^e 117 ^e	110 47100	0.69 -	0.32 -	32	430
206	3HPL-96 ^g CTI	4.0	77 -40	64 2280 ^e	483 122 ^e	483 122 ^e	62 38500	0.19 -	0.24 -	36	620
207	3HPL-96 ^g CTI	6.0	77 -40	28 1770 ^e	568 ^e 14 ^e	570 ^e 14 ^e	40 36100	0.08 -	0.11 -	63	900
209	3HPL-97 ^g CTI	4.0	77 -40	81 1365 ^e	495 126 ^e	531 ^e 127 ^e	132 6000	0.16 -	1.02 -	17	45
211	11.8AH CTI	4.0	77 -40	17 1,05 ^e	198 368 ^e	200 368 ^e	17 344	0.19 2.66	0.02 1.13	24	20
212R	11.8A CTI	4.0	77 -40	14 159	260 557	260 557	13 95	0.11 0.24	0.04 0.64	11	7

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Table VI

COMPOSITION^a AND PROPERTIES OF TELAGEN S BINDERS

Composition		Mechanical Properties						Ratio of Mech. Prop. at -40° to 77°F			Gel Fraction	Crosslink Density ^c Moles Chain/cc x 10 ⁵
Prepolymer Crosslinker	HDI/CTI ^b	Temp Of	σ_m psi	ϵ_m %	σ_b %	E _o psi	C ₁ Kg/cm ²	C ₂ Kg/cm ²	σ	E _o	C ₁	
148AH/148A ^d CTI	3.0	77 -40	9 310 ^e	480 410 ^e	480 -	4 268	0.41 1.96	0.042 1.45	34	67	5	0.24
25.7 CTI	3.0	77 -40	3 ^e 175	740 ^a 526	- 528	7 158	0.009 0.48	0.003 1.01	58	23	53	0.08
148AH/25.7 ^f CTI	3.0	77 -40	22 303 ^e	310 382 ^e	315 385 ^e	19 208	0.17 1.38	0.012 0.76	14	11	8	1.40
3HPL-96 CTI	4.0	77 -40	15 554 ^e	360 335 ^e	360 339 ^e	11 553	0.075 2.95	0.042 2.10	37	50	39	0.91
3HPL-97 CTI	3.5	77 -40	46 785 ^e	500 343 ^e	500 345 ^e	42 1136	0.13 2.60	0.30 9.00	17	27	20	0.88
3HPL-96 ^g CTI	2.0	77 -40	79 2500 ^e	214 117 ^e	214 117 ^e	110 47100	0.69 -	0.32 -	32	430	-	5.00
3HPL-96 ^g CTI	4.0	77 -40	64 2280 ^e	483 122 ^e	483 122 ^e	62 38500	0.19 -	0.24 -	36	620	-	1.43
3HPL-96 ^g CTI	6.0	77 -40	28 1770 ^e	568 14 ^e	570 14 ^e	40 36100	0.08 -	0.11 -	63	900	-	0.24
3HPL-97 ^g CTI	4.0	77 -40	81 1365 ^e	495 126 ^e	531 127 ^e	132 6000	0.16 -	1.02 -	17	45	-	0.28
148AH CTI	4.0	77 -40	17 4105 ^e	198 368 ^e	200 368 ^e	17 344	0.19 2.66	0.02 1.13	24	20	14	1.07
148A CTI	4.0	77 -40	14 159	260 557	260 557	13 95	0.11 0.24	0.04 0.64	11	7	2	1.1

B

Table VI (Cont.)

Reference No.	Prepolymer Crosslinker	Composition HDI/CTI ^b	Mechanical Properties					Ratio of Mech. Prop. at -40° to 77°	
			Temp °F	σ_m psi	ϵ_m %	ϵ_b %	E_o psi	C_1 Kg/cm ²	C_2 Kg/cm ²
213	148A/148AH ^h CTI	3.95	77 -40	18 272 ^e	265 421 ^e	265 423 ^e	20 246	0.15 0.73	0.03 1.05
214	148A/148AH ^h CTI	3.90	77 -40	19 215 ^e	332 ^e	332 ^e	20 181	0.12 1.05	0.04 1.83
215	148A/148AH ^h CTI	3.85	77 -40	23 489	300 414	300 414	21 372	0.17 2.35	0.04 1.98
216	148A/148AH ^h CTI	3.80	77 0	16 468	298 315	298 317	20 475	0.11 3.20	0.05 2.15
217	148A CTI	3.75	77 -40	27 362	330 338	330 338	22 383	0.17 1.65	0.05 1.95
218A	148AH CTRO	4.0 ^{b,i}	77 -40	16 580	353 381	-	16 1435	0.090 -	0.059 -
219	148AH CTRO	4.0 ^{b,j}	77 -40	6 ^e 381	556 ^e 481	-	15 315	0.025 -	0.007 -
219A	148AH CTRO	4.0 ^{b,i,j}	77 -40	11 ^e 370	630 ^e 488	-	62 273	0.024 -	0.028 -
224	148AH CTRO	4.0 ^{b,i,j,k}	77 -40	17 406 ^e	452 473 ^e	-	10 306	0.055 -	0.062 -
225	148AH CTRO	4.0 ^{b,i,k}	77 -40 -75	14 356 ^e 1083 ^e	265 407 ^e 202 ^e	-	11 312 2293	0.117 1.83 -	0.09 1.88 -
226	148AH CTRO	4.0 ^{b,i,l}	77 -40 -75	17 362 ^e 1238 ^e	226 386 ^e 204 ^e	-	20 273 1922	0.150 1.85 -	0.05 1.65 -

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Cont)

Composition		Mechanical Properties							Ratio of Mech. Prop. at -40° to 77°F			Grosslink Density ^c Moles Chain/cc x 10 ⁵
Prepolymer Crosslinker	HDI/CTI ^b	Temp °F	σ _m psi	ε _m %	ε _b %	E _o psi	C ₁ Kg/cm ²	C ₂ Kg/cm ²	σ	E _o	Gel Fraction	
1L8A/1L8AH ^h CTI	3.95	77 -40	18 272 ^e	265 421 ^e	265 423 ^e	20 246	0.15 0.73	0.03 1.05	15	12	0.055	0.91
1L8A/1L8AH ^h CTI	3.90	77 -40	19 215 ^e	332 -	332 ^e -	20 181	0.12 1.05	0.04 1.83	11	9	0.051	0.77
1L8A/1L8AH ^h CTI	3.85	77 -40	23 489	300 414	300 414	21 372	0.17 2.35	0.04 1.98	21	18	0.061	1.12
1L8A/1L8AH ^h CTI	3.80	77 -40	16 468	298 315	298 317	20 475	0.11 3.20	0.05 2.15	29	24	0.053	0.85
1L8A CTI	3.75	77 -40	27 362	330 338	330 338	22 383	0.17 1.65	0.05 1.95	13	17	0.064	1.23
1L8AH CTRO	4.0 ^{b,i}	77 -40	16 580	353 391	- -	16 435	0.090 -	0.059 -	36	27	0.054	0.88
1L8AH CTRO	4.0 ^{b,j}	77 -40	6 ^e 381	556 ^e 481	- -	15 315	0.025 -	0.007 -	63	21	0.026	0.21
1L8AH CTRO	4.0 ^{b,i,j}	77 -40	11 ^e 370	630 ^e 488	- -	62 273	0.024 -	0.028 -	34	4	0.030	0.28
1L8AH CTRO	4.0 ^{b,j,k}	77 -40	17 406 ^e	452 173 ^e	- -	10 306	0.055 -	0.062 -	24	31	0.047	0.67
1L8AH CTRO	4.0 ^{b,i,k}	77 -40 -75	14 356 ^e 1083 ^e	265 407 ^e 202 ^e	- - -	11 312 2293	0.117 1.83 -	0.09 1.88 -	25	28	0.058	1.02
1L8AH CTRO	4.0 ^{b,i,l}	77 -40 -75	17 362 ^e 1238 ^e	226 346 ^e 204 ^e	- - -	20 273 1922	0.150 1.85 -	0.05 1.65 -	21	14	0.079	1.27

R

Table VI (Cont)

Reference No.	Composition		Mechanical Properties						Ratio of Mech. Prop. at -400 to 77°	
	Prepolymer Crosslinker	HDI/CTI ^b	Temp °F	C _m psi	ε _m %	ε _b %	E _o psi	C ₁ ² Kg/cm ²	C ₂ ² Kg/cm ²	$\frac{r}{E_o}$
228	25.7	GTR0 4.0 ^{b,i}	77 -40 -75	21 287 1018 ^e	654 582 268 ^e	- - -	10 110 1333	0.065 0.56 -	0.027 0.88 -	14 11
229	25.7	GTR0 4.0 ^{b,i,j}	77 -40 -75	4 ^e 28 ^e 382	700 ^e 727 ^e 447	- - -	2 82 503	0.020 0.07 -	0.003 0.32 -	7 41
232	3HPL-90	GTR0 4.0 ^{b,i}	77 -40 -75	18 ^e 150 ^e 626 ^e	714 ^e 728 ^e 670 ^e	- - -	16 110 235	0.041 0.28 -	0.156 1.15 -	8 7
233	3HPL-90	GTR0 4.0 ^{b,i,j}	77 -40 -75	3 ^e 64 ^e 334 ^e	709 ^e 730 ^e 690 ^e	- - -	4 52 197	0.009 0.16 -	0.032 0.39 -	21 13
234	3HPL-90	GTR0 2.33 ^{b,i,j}	77 -40 -75	17 ^e 90 ^e 399 ^e	710 ^e 727 ^e 665 ^e	- - -	12 82 219	0.044 0.22 -	0.060 0.74 -	5 7
235	14.8AH	GTR0 1.5 ^{b,i,j}	77 -40 -75	20 177 ^e 964 ^e	115 340 276 ^e	- - -	32 108 800	0.338 1.01 -	0.050 0.26 -	9 3
239	3HPL-90	CTI 4.00	77 -40	7 96	716 714	716 715	8 92	.014 .33	.072 .66	14 11
239 ^m	3HPL-90	CTI 4.00	77 -40	18 128	712 715	712 716	17 101	.046 .27	.063 .94	7 6
240	3HPL-90	CTI 3.75	77 -40	17 116	720 714	720 715	15 92	.043 .38	.122 .70	7 6
240 ^m	3HPL-90	CTI 3.75	77 -40	22 128	720 700	720 700	17 99	.043 .36	.122 .59	6 6
241	3HPL-90	CTI 3.50	77 -40	13 115	711 716	720 716	14 99	.010 .40	.120 .66	9 7

Composition		Mechanical Properties							Ratio of Mech. Prop. at -40° to 77°F			Gel Fraction	Crosslink Density Moles Chain/cc x 10 ⁵	
Polymer Slurker	HDI/CTI ^b	Temp °F	σ_m psi	σ_m %	ϵ_b %	E _o psi	C ₁ ² Kg/cm ²	C ₂ ² Kg/cm ²	σ	E _o	C ₁			
GTRO	4.0 ^{b,i}	77 -40 -75	21 287 1018 ^e	654 582 268 ^e	- - -	- - -	10 110 1333	0.065 0.56 -	0.027 0.88 -	14	11	9	0.047	0.67
GTRO	4.0 ^{b,i,j}	77 -40 -75	4 ^e 28 ^e 382	700 ^e 727 ^e 447	- - -	- - -	2 82 503	0.020 0.07 -	0.003 0.32 -	7	41	4	0.018	0.10
GTRO	4.0 ^{b,i}	77 -40 -75	18 ^e 150 ^e 626 ^e	714 ^e 728 ^e 670 ^e	- - -	- - -	16 110 235	0.041 0.28 -	0.156 1.15 -	8	7	7	0.027	0.23
GTRO	4.0 ^{b,i,j}	77 -40 -75	3 ^e 64 ^e 334 ^e	709 ^e 730 ^e 690 ^e	- - -	- - -	4 52 197	0.009 0.16 -	0.032 0.39 -	21	13	18	0.014	0.06
GTRO	2.33 ^{b,i,j}	77 -40 -75	17 ^e 90 ^e 399 ^e	710 ^e 727 ^e 665 ^e	- - -	- - -	12 82 219	0.044 0.22 -	0.060 0.74 -	5	7	5	0.062	1.15
GTRO	1.5 ^{b,i,j,1}	77 -40 -75	20 177 964 ^e	115 340 276 ^e	- - -	- - -	32 108 800	0.333 1.01 -	0.050 0.26 -	9	3	3	0.094	2.6
CTI	4.00	77 -40	7 96	716 714	716 715	8 92	- -	.014 .33	.072 .66	14	11	24	0.021	0.14
CTI	4.00	77 -40	18 128	712 715	712 716	17 101	- -	.046 .27	.063 .94	7	6	6	0.032	0.32
CTI	3.75	77 -40	17 116	720 714	720 715	15 92	- -	.043 .38	.122 .70	7	6	9	0.031	0.31
CTI	3.75	77 -40	22 128	720 700	720 700	17 99	- -	.043 .36	.122 .58	6	6	8	0.034	0.36
CTI	3.50	77 -40	13 115	711 716	720 716	14 99	- -	.010 .40	.120 .66	9	7	10	0.027	0.22

RB

Table VI (Cont)

Reference No.	Prepolymer Crosslinker	Composition HDI/CTI ^b	Mechanical Properties					Ratio of Mech. Prop. at -100 to 77°F		
			Temp °F	σ _m psi	ε _m %	ε _b %	E _o psi	C ₁ ² Kg/cm ²	C ₂ ² Kg/cm ²	σ / E _o / C ₁ / F
241R ^m	3HPL-90 CTI	3.50	77 -40	23 132	713 694	713 696	19 92	.61 .38	.158 .46	6 5 6
242	3HPL-90 CTI	3.00	77 -40	26 139	694 714	696 715	19 101	.067 .51	.170 .62	5 5 8
242R ^m	3HPL-90 CTI	3.00	77 -40	11 148	716 713	716 714	7 92	.031 .56	.56 .62	13 12 18
243 ^m	3HPL-125 CTI	4.00	77 -40	6 400	705 501	705 502	16 410	.009 1.70	.027 4.30	67 26 189
244 ^m	3HPL-125 CTI	3.75	77 -40	9 428	709 513	712 515	7 394	.021 1.75	.026 3.90	46 56 83
245 ^m	3HPL-125 CTI	3.50	77 -40	8 409	706 513	763 513	6 383	.022 1.55	.023 4.41	54 64 70
246 ^m	3HPL-125 CTI	3.00	77 -40	19 506	708 533	710 533	29 437	.045 1.85	.046 3.90	19 15 41
247 ^m	3HPL-123 CTI	4.00	77 -40	5 56	707 714	707 725	2 110	.012 .19	.009 .14	11 69 16
248 ^m	3HPL-123 CTI	3.75	77 -40	3 47	675 715	675 716	2 66	.008 .10	.004 .40	16 33 12
249 ^m	3HPL-123 CTI	3.50	77 -40	10 75.8	705 716	716 717	3 73	.030 .18	.013 .41	8 23 6
250 ^m	3HPL-123 CTI	3.00	77 -40	9 89	500 713	500 714	2 77	.025 .21	.052 .44	10 34 8
251 ^m	169 CTI	4.00	77 -40	7 47	706 711	706 714	6 55	.007 .10	.030 .29	6 9 14

A

Cont)

Composition		Mechanical Properties							Ratio of Mech. Prop. at -100° to 77°F			Gel Fraction	Crosslink Density ^c Moles Chain/cc x 10 ⁵
Prepolymer Crosslinker	HDI/CTI ^b	Temp °F	σ _m psi	ε _m %	σ _b %	E _o psi	C ₁ Kg/cm ²	C ₂ Kg/cm ²	σ	E _o	C ₁		
3HPL-90	CTI	77 -40	23 132	713 694	713 696	19 92	.61 .38	.158 .46	6	5	6	.037	0.41
3HPL-90	CTI	77 -40	26 139	694 714	696 715	19 101	.067 .51	.170 .62	5	5	8	.041	0.50
3HPL-90	CTI	77 -40	11 148	716 713	716 714	7 92	.031 .56	.56 .62	13	12	18	.036	0.40
3HPL-125	CTI	77 -40	6 400	705 501	705 502	16 410	.009 1.70	.027 4.30	67	26	189	.022	0.15
3HPL-125	CTI	77 -40	9 428	709 513	712 515	7 394	.021 1.75	.026 3.90	46	56	83	.028	0.24
3HPL-125	CTI	77 -40	8 409	706 513	763 513	6 383	.022 1.55	.023 4.41	54	64	70	.027	0.23
3HPL-125	CTI	77 -40	19 506	708 533	710 533	29 437	.045 1.85	.046 3.90	19	15	41	.038	0.44
3HPL-123	CTI	77 -40	5 56	707 714	707 725	2 110	.012 .19	.009 .14	11	69	16	.021	0.13
3HPL-123	CTI	77 -40	3 47	675 715	675 716	2 66	.008 .10	.004 .40	16	33	12	.018	0.10
3HPL-123	CTI	77 -40	10 75.8	705 716	716 717	3 73	.030 .18	.013 .41	8	23	6	.029	0.26
3HPL-123	CTI	77 -40	9 89	500 713	500 714	2 77	.025 .21	.052 .44	10	34	8	.034	0.35
169	CTI	77 -40	7 47	706 711	706 714	6 55	.007 .10	.030 .29	6	9	14	.024	0.18

B

Table VI (Cont)

Reference No.	Prepolymer Crosslinker	HDI/CTI ^b	Mechanical Properties					Ratio of Mech. Prop at -40° to 77° F	
			Temp °F	σ_m psi	ϵ_m %	ϵ_b %	E_o psi	C_1 $\frac{kg}{cm^2}$	C_2 $\frac{kg}{cm^2}$
252 ^m	169	CTI	77 -40	12 71	480 716	552 716	6 55	.032 .09	.045 .44
253 ^m	169	CTI	77 -40	11 63	571 715	573 719	6 51	.030 .09	.030 .42
254 ^m	169	CTI	77 -40	12 89	450 712	450 712	8 59	.033 .13	.060 .13
255 ^m	3HPL-90	E-246	77 -40	10 87	523 643	523 643	13 93	.030 .20	.098 .76
257 ^m	3HPL-90	PAPI	77 -40	10 91	719 644	719 644	9 82	.029 .35	.062 .60
258	3HPL-90	PAPI	77 -40	2 64	711 644	- -	6 70	.004 .13	.024 .66
260 ^m	3HPL-90	GTRC/ PAPI	77 -40	9 107	721 660	720 664	10 142	.021 .45	.068 .54

^aThe binders have NCO/OH=1.0, 25% IDP, and 0.0208% FeAA (.05% for binders containing GTRC 218A-235) unless otherwise stated cured 6 days at 135°F; the others, 7 days at 135°F.

^bWhere another isocyanate replaced CTI, this equivalents ratio is the isocyanate to HDI ratio. In cases where CTRO replaced prepolymer + other diols) to CTRO ratio is given. Where HDI is replaced with DDI the equivalents ratio is DDI to CTI.

^cDerived from gel fraction (Figure 26, Report AFRPL-TR-67-158); when gel fraction not available derived from 10-4 C₁.

^d148AH/148A = 2.0.

^eLimit of crosshead or tab failure.

^f148AH/25.7 = 1.0.

^gContains no plasticizer.

^h148A/148AH = 4.0, 1.5, 0.67, 0.25 respectively for Binder 213, 214, 215, and 216.

ⁱNCO/OH = 1.05.

^jHDI replaced by DDI.

^kContains Polycrin 51; 148AH/Polycrin 51 = 3.0.

^lContains Polycrin 23; 148AH/Polycrin 23 = 3.0 and 2.0 for Binders 226 and 235 respectively.

^mContains 0.0312% FeAA.

ⁿ3HPL-90/GTRO.

22nt)

Prepolymer Crosslinker	HDI/CTI ^b	Mechanical Properties							Ratio of Mech. Prop. at -100° to 77°F			Gel Fraction	Crosslink Density ^c Moles Chain/cc x 10 ⁵
		Temp °F	σ_m psi	ϵ_m %	ϵ_b %	E_o psi	C_1 ² Kg/cm ²	C_2 ² Kg/cm ²	σ	E_o	C_1		
169 CTI	3.75	77 -40	12 71	460 716	552 716	6 55	.032 .09	.045 .44	6	9	3	.032	0.32
169 CTI	3.50	77 -40	11 63	571 715	573 719	6 51	.030 .09	.030 .42	6	8	3	.031	0.30
169 CTI	3.00	77 -40	12 89	450 712	450 712	8 59	.033 .13	.060 .43	8	7	4	.036	0.40
3HPL-90 E-246	2.00 ^b	77 -40	10 87	523 643	523 643	13 93	.030 .20	.098 .76	9	7	7	-	0.30
3HPL-90 PAPI	2.00 ^b	77 -40	10 91	719 644	719 644	9 82	.029 .35	.062 .60	9	9	11	.026	0.21
3HPL-90 PAPI	3.00 ^b	77 -40	2 64	711 644	- -	6 70	.004 .13	.024 .66	30	12	32.5	.013	0.05
3HPL-90 CTRO/ PAPI	3.00 ⁿ	77 -40	9 107	721 660	720 664	10 142	.021 .45	.068 .54	11	14	21.4	.025	0.19

have NCO/OH=1.0, 25% IDP, and 0.0206% FeAA (.05% for binders containing GTR 218A-235) unless otherwise stated. Binders 200-217 were at 135°F; the others, 7 days at 135°F.

isocyanate replaced CTI, this equivalents ratio is the isocyanate to HDI ratio. In cases where GTR replaced CTI, the prepolymer (or other diols) to CTRO ratio is given. Where HDI is replaced with DDI the equivalents ratio is DDI to CTI.

gel fraction (Figure 26, Report AFRPL-TR-67-158); when gel fraction not available derived from 10⁻⁴ C₁.

2.0.

shear or tab failure.

1.0.

plasticizer.

4.0, 1.5, 0.67, 0.25 respectively for Binder 213, 214, 215, and 216.

by DDI.

cin 51: 1.5AH/Polycin 51 = 3.0.

cin 23: 1.5AH/Polycin 23 = 3.0 and 2.0 for Binders 226 and 235 respectively.

12% FeAA.

B

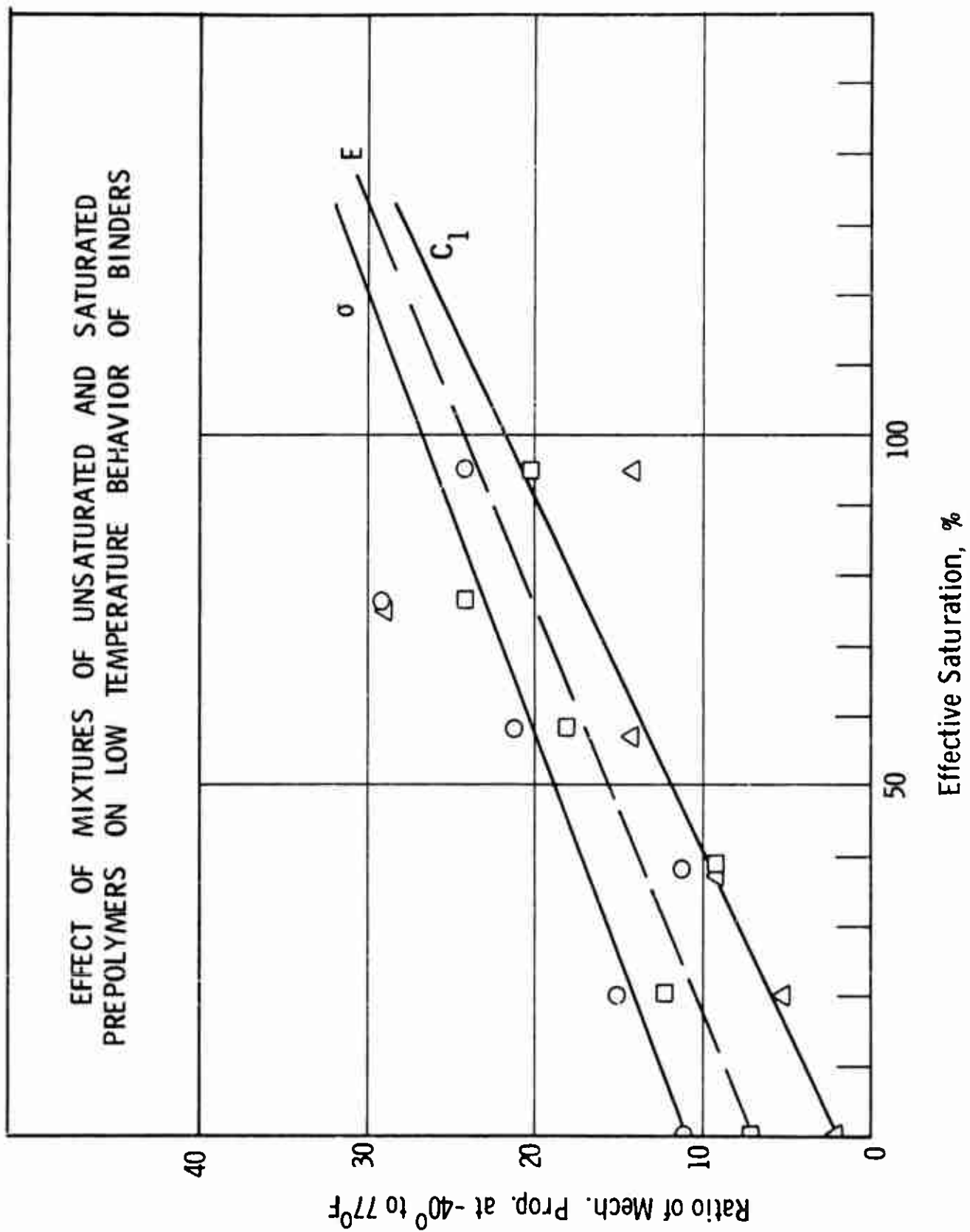
previous quarter, the complete property data for which have become available. For assessing the low temperature behavior of binders, the criterion has been the ratio of a mechanical property such as break tensile, initial modulus, or C_1 at -40°F to that at 77°F . The lower this ratio the better will be the low temperature properties of a binder and hence, of a propellant. Previous work has indicated that over the temperature range 150° to -75°F propellant moduli are fifty times the corresponding binder moduli.

(2) Effect of Saturation

During the previous quarter, the very significant influence of saturation on low temperature properties was indicated. This work was not conclusive because the prepolymer molecular weight was not controlled. The work of the previous quarter was confirmed with a series of prepolymers of the same molecular weight ranging in saturation from 0 to 93%. The conclusion that saturation of functionally terminated polybutadienes adversely affects low temperature behavior of binders made from these materials was firmly established.

A series of binders (212-217) with varying ratios of unsaturated (148A) and saturated (148AH) prepolymers were prepared to compare such compositions with that prepared from a partially hydrogenated prepolymer such as 3HPL-90. The C_1 and gel fraction data indicate binders of approximately equal crosslink density. In general, the properties at 77°F are similar. At -40°F , better elongation and lower moduli were obtained with those compositions wherein the concentration of the unsaturated prepolymer was higher than that of the saturated. None of the compositions had as low an increase in modulus from 77° to -40°F as Binder 193 (3 fold) which was prepared from the partially hydrogenated Prepolymer 3HPL-90. The variation of the change in properties as the temperature is decreased from 77°F to -40°F is indicated in Table VII and in Figure 4. The conclusion is drawn that a mixture of saturated and unsaturated prepolymers is not as effective as a partially saturated one for attaining low temperature properties.

Further studies were made with three prepolymers of equal molecular weight and varying saturation. These prepolymers have nearly the same equivalent weight since two of them, 3HPL-123 (60% saturated) and 3HPL-125 (93% saturated), were derived by hydrogenation of the third, 242AM-169 (unsaturated). The previously characterized prepolymer, 3HPL-90 (54% saturated), having twice the equivalent weight was used to prepare controls for the evaluation. The HDI to CTI equivalents ratios were varied within each series to obtain a range of crosslink densities. The binders were swelled with toluene to obtain gel fractions. Crosslink densities were calculated for several binders from compression moduli of the swelled networks. Aging studies have been initiated to determine the oxidative stability of these binders prepared from partially saturated prepolymers.



-61-

Figure 4

Table VII

EFFECT OF MIXTURES OF UNSATURATED AND SATURATED PREPOLYMERS
ON LOW TEMPERATURE BEHAVIOR OF BINDERS^a

Reference No.	Prepolymers	Saturated to Unsaturated Eq. Ratio	Effective Saturation %	Ratio of Mech. Prop. at 40° to 77°F		
				σ	E_o	C_1
212R	148A	0	0	11	7	2
213	148A/148AH	0.25	20	15 ^b	12	5
214	148A/148AH	0.67	38	11 ^b	9	9
215	148A/148AH	1.50	57	21	18	14
216	148A/148AH	4.0	76	29	24	29
211	148AH	∞	95	24 ^b	20	14
242	3HPL-90 ^c	-	54	5	5	8

^aComposition of binders given in Table VI.

^bThese values for doubtful because of tab failures at -40°F testing.

^cPartially saturated prepolymer.

The mechanical properties of the cured binders listed in Table VI reflect the differences in the degree of saturation of the new prepolymers. The tensile strengths, moduli and C_1 values of the binders containing the unsaturated prepolymer 242AM-169 (Binders 251 to 254) increased 3 to 14 fold from 77° to -40°F. These values were slightly lower than those obtained with Binders 239R to 242R containing the 55% saturated Prepolymer 3HPL-90 which has over twice the equivalent weight. Binders 247 to 250 containing the 60% saturated Prepolymer 3HPL-123 gave tensile strength and C_1 values increases averaging about 11 fold, moduli increases were higher. The very low modulus values of these soft bars may have resulted in measurement errors giving rise to the abnormally high modulus increase. The tensile increase did not differ greatly from those for Binders 251 to 254. Increase

of moduli, tensile strengths and C_1 values (ignoring that for Binder 243) for Binders 243 to 246 prepared with the 93% saturated Prepolymer 3HPL-125) averaged about 50 fold indicating inferior low temperature behavior. The results indicate that the low temperature properties can be improved by using a prepolymer with about 60% saturation. This can be seen more graphically in Figure 5.

The mechanical properties change very little for 0 to 60% saturation, but the subsequent changes are more pronounced. The final choice of a prepolymer will, however, require a knowledge of variation of oxidative stability with saturation. These experiments are in progress.

(3) Effect of Prepolymer Molecular Weight

An original postulate for the poor low temperature behavior of saturated binders was that the relatively low molecular weight of the saturated prepolymers resulted in high polar group concentrations and that these groups associated at low temperature. Data supported this postulate (see Report AFRPL-TR-67-260) but not unambiguously. No effort to clear this ambiguity was made because the effect, if it existed or not, was overshadowed by the very pronounced effect of saturation on the low temperature properties. However comparison of binders made from 3HPL-90 (54% saturated, molecular weight 4200) with those made from 3HPL-123 (60% saturated, molecular weight 1630) indicate better low temperature properties with the higher molecular weight prepolymer. Thus for Binders 239 to 242R made with Prepolymer 3HPL-90 the ratios of properties at -40° to those at 77°F are: σ , 8; E_0 , 7; and C_1 , 15 while for Binders 247 to 250 made with Prepolymer 3HPL-123, the ratios are: σ , 11; E_0 , 40; and C_1 , 11.

This means that since a less saturated prepolymer has a lower viscosity, the prepolymer can be made to a higher molecular weight than those of the current saturated prepolymers. As a result there will be an improvement in propellant properties not only because of the greater unsaturation but also because of the greater molecular weight.

(4) Effect of Crosslinker or Curing Agents

Variation of the crosslinker or curing agent did not greatly affect low temperature properties. This is discussed more completely in Section IV.A.7.

c. Propellant Studies

(1) General

One-pound batches of propellants having binders crosslinked with polyisocyanates or with glycerol triricinoleate (GTRO)

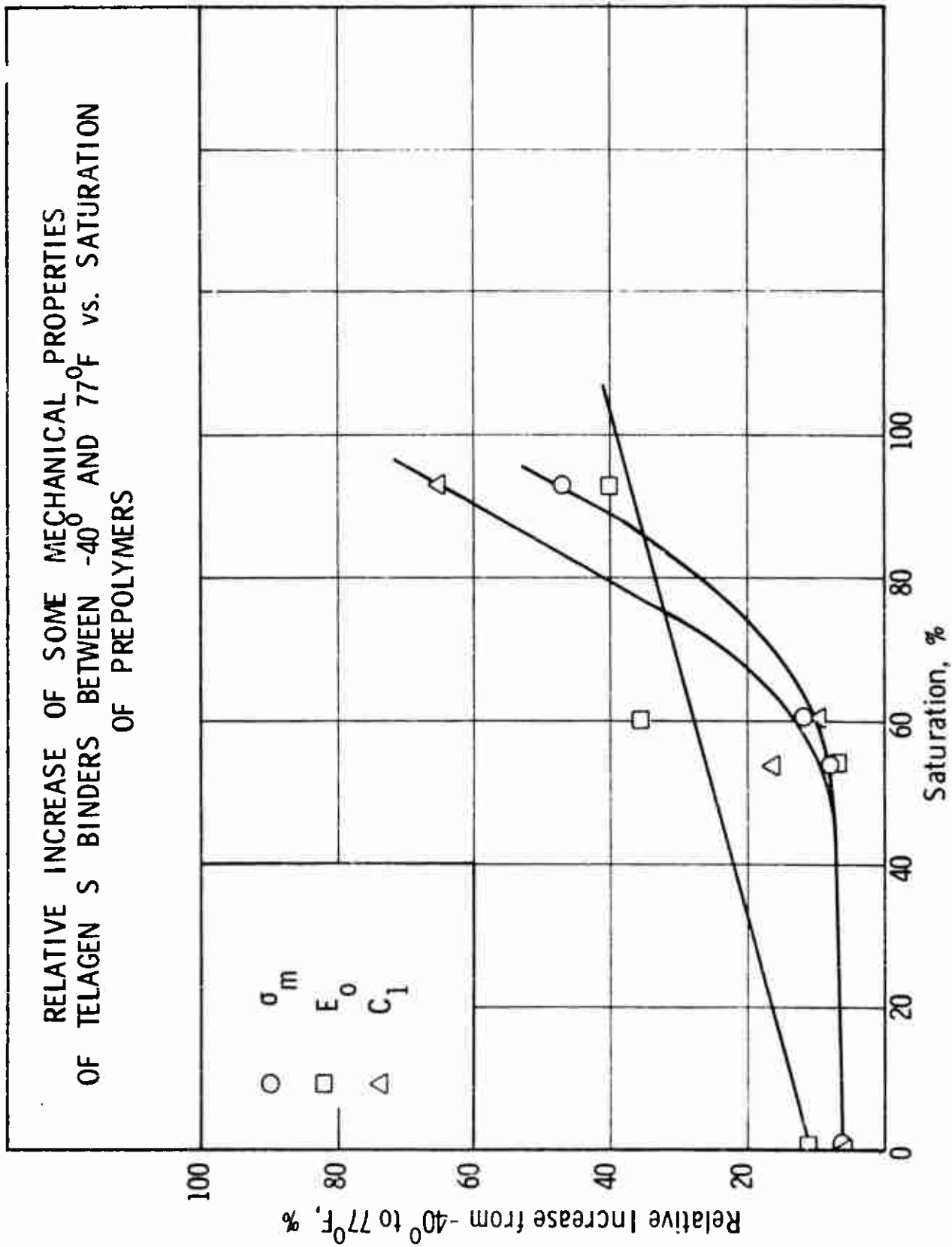


Figure 5

were prepared for evaluation of low temperature properties. In the polyisocyanate cured system, diisocyanate DDI-1410 (General Mills) and hexamethylene diisocyanate (HDI), were used as chain extenders, and these systems were crosslinked with CTI or PAPI. The compositions and properties of the propellants are given in Table VIII. DDI and HDI were used in the systems crosslinked with CTRO (Table IX).

(2) Polyisocyanate Systems

(a) Effect of Unsaturation

Better low temperature mechanical properties were very evident for propellants made with the partially saturated prepolymer 3HPL-90 (Batches 3689, 3690, 4347, 4348). Mixtures of saturated and unsaturated prepolymers (148AH and 148A, Batch 3691) had better low temperature mechanical behavior than completely unsaturated systems, but the magnitude of the improvement was not great. While comparisons involving Prepolymers 3HPL-90 with 148A or AH must take into account the differences in molecular weight (4160 for 3HPL-90 and 1750 for 148A), the molecular weight exerted only a minor influence on the low temperature behavior of saturated binder propellants.

(b) Effect of Prepolymer Molecular Weight

The properties of Batches IGP-2888 and 2888R, which indicate the good reproducibility of these propellants, were compared with those of Batch IGP-4100; the former were prepared with a saturated prepolymer of 990 molecular weight, the latter, with a saturated prepolymer of 1780 molecular weight. There was no significant difference in mechanical properties between the two propellant formulations at ambient or at -75°F. The binder studies indicated only slight, if any, improvement of mechanical properties could be expected by this increase of prepolymer molecular weight. Further increase of molecular weight of a saturated prepolymer is not consistent with low viscosity and good processability.

(c) Effect of Isocyanate Type

Comparison of Batches 4100 and 4102 indicated that the use of the relatively long chain diisocyanate, DDI-1410, did not improve low temperature properties. This was shown by the increase in -75° to 77°F moduli ratio (76 for the propellant with HDI and 148 for that with DDI).

PAPI might be a suitable substitute for CTI as indicated by the data for Batches 3689, 3690, and 4100. The low temperature properties and the moduli ratio at -75° to 77°F were the same for a given prepolymer, and PAPI cured propellants showed only slightly inferior properties at ambient temperatures. The greater elongation obtained by use of PAPI was probably due to the lower moduli of propellants containing this isocyanate.

Table VIII

COMPOSITIONS^a AND PROPERTIES OF PREPOLYMER PREPARED WITH TELACEN S PREPOLYMERS

Reference No., IGP-	Composition				Hardness ^b Shore A	Mechanical Properties						E _{-75/E77}	
	Prepolymer	Isocyanate	Isocyanate Ratio	NCO/OH		Temp, °F	σ _b		ε _b		σ _a		
							psi	psi	%	%	psi		psi
2888	3HPL-96	HDI/CTI	4	1.02	64	61	77 -75	129 1205	- -	25 3	31 3	758 58460	77
2888R	3HPL-96	HDI/CTI	4	1.02	58	77	77 -40 -75	125 882 1243	123 877 1243	23 4 3	27 6 3	890 30520 56120	63
3689	3HPL-90	HDI/CTI	4	1.02	61	70	77 -75	141 703	138 703	30 6	33 6	1054 20240	20
3690	3HPL-90	HDI/PAPI	4	1.02	65	78	77 -75	118 789	114 782	39 8	46 10	682 18370	27
3691	1L8AH ^c 1L8A	HDI/PAPI	4	1.02	53	70	77 -75	145 948	145 948	20 4	21 4	1003 37980	38
3945	1L8AH	DDI/PAPI	4	1.05	27	43	77 -40 -75	61 623 625	60 614 625	24 7 1	25 8 1	328 13780 25000	76
4100	1L8AH	HDI/CTI	4	1.02	64	72	77 -40 -75	131 771 1124	131 771 1124	25 5 3	26 5 3	756 29590 57500	76
4102	1L8AH	DDI/CTI	4	1.02	36	44	77 -40 -75	65 632 803	65 630 803	32 8 2	35 8 2	291 13965 43000	148
4103	1L8AH ^d	DDI/CTI	4	1.02	47	55	77 -40 -75	96 697 1377	94 697 1377	33 5 1	36 5 1	413 18191 102000	248
4347	3HPL-90	HDI/CTI	5.0	1.02	70	78	77 -40 -75	82 399 663	81 379 655	40 16 9	43 32 12	463 5203 12980	28
4348	3HPL-90	HDI/CTI	4.5	1.02	71	84	77 -40 -75	146 508 678	145 504 675	42 15 10	46 17 11	734 6038 11980	16

please see footnote on next page.

Please see footnote on next page.

^aAll propellants contained 88% solids, 3% IDP (except for IGP-4103), C-1, HAA, and FeAA and were cured at 135°F for 7 days.

^bFifteen-second readings.

^cPrepolymers at 1 to 1 equivalence ratio.

^d1.8% IDP.

Table IX

COMPOSITIONS^a AND PROPERTIES OF TELAGEN S PROPELLANTS CROSSLINKED WITH GTRO

Reference No., IGP-	Prepolymer	Composition		Hardness ^c Shore A	Mechanical Properties							
		Isocyanate	Equiv. Ratio ^b		Temp, °F		σ_b		ϵ_b		E_o psi	E_{-75}/E_{77}
					psi	psi	psi	psi	%	%		
3835	148AH	HDI	.7/.3/1.05	78 78	77 -75	230 1133	230 1130	17 3	17 3	1763 54528	31	
3836	25.7	HDI	.7/.3/1.05	20 25	77 -75	52 1029	49 1029	47 5	60 5	169 36141	214	
3837	3HPL-90	HDI	.7/.3/1.05	52 70	77 -75	148 685	146 681	36 10	41 12	699 11967	17	
3838	3HPL-90	DDI	.7/.3/1.05	37 45	77 -75	73 620	70 537	27 6	34 13	575 19785	35	
3944	148AH	DDI	.7/.3/1.05	40 48	77 -40 -75	63 432 912	63 423 876	18 7 3	19 8 3	498 10723 39657	80	
3946	148AH	DDI/PAPI	.8/.2/.1	15 22	77 -40 -75	31 503 865	31 501 856	24 6 3	24 7 3	149 11640 29590	200	
4349	3HPL-90	HDI	.8/.2/1.05	65 68	77 -40 -75	108 432 669	106 425 656	36 26 9	39 32 11	664 5340 13616	20	

^aAll propellants contained 88% solids, 3% IDP, C-1, NAA, and FeAA, and were cured at 135°F for 7 days.^bEquivalents ratio of prepolymer/GTRO/Diisocyanate(s).^c15 second readings.

(d) Effect of Plasticizer Concentration

Data from Batch 4103, which contained 1.8% IDP instead of 3%, were interesting. Although the properties at 77°F showed the propellant to be relatively soft (low modulus and hardness), the low temperature properties are very poor, and the ratio of moduli at -75° to 77°F is very high (248). These results seemingly support the contention that IDP helps achieve better low temperature properties.

(3) GTR0 Crosslinked Systems

(a) General

Binder studies indicated that GTR0 might serve as a suitable low cost substitute for OTI. The data in Table IX strongly support this conclusion and suggest further investigation of the GTR0 crosslinked systems.

(b) Effect of Unsaturation

Significantly better low temperature properties are attained with the partially saturated prepolymer, 3HPL-90, than with the saturated prepolymer, 148AH (compare Batch 3835 with 3837 and 3838 with 3944). The best balance of properties was obtained with 3HPL-90, GTR0 and HDI (Batch 3837). The low temperature properties of these propellants may be even further improved by decreasing the ambient modulus of the propellants to about 450.

(c) Effect of Isocyanate Type

As with the polyisocyanate crosslinked systems, the use of DDI was disadvantageous (Compare Batch 3835 with 3944 and 3837 with 3838), compared to HDI. Since the functionality of DDI-1410 is 2.06, the difficulty may be a low extent of reaction. Better elongation at maximum stress (ϵ_m) and lower ratio of moduli at -75° to 77°F were obtained with HDI. Partial substitution of a polyisocyanate (PAPI) for triol was deleterious (Batch 3946).

(d) Effect of Crosslink Ratio

An attempt to decrease the modulus and crosslink density of the propellant by increasing the prepolymer to GTR0 ratio caused only a minor change of the ambient modulus (compare Batch 3837 with 4349). The reason for this small change is not known at present and requires further investigation.

(e) Effect of Pendant Ethyl Groups

Batch 3836 was prepared with a saturated prepolymer containing a high concentration (66%) of pendant ethyl groups. High ratio of moduli at -75° to 77°F and poor overall mechanical properties were obtained.

7. Replacement of CTI

During this quarter more emphasis was placed on the testing of substitutes for CTI. Much of this work was coupled with the study of low temperature properties and was reported in previous sections of this report. The substitutes were tested in binders and propellants so that the data are reported in Tables VI, VIII, and IX. Glycerin triricinoleate, E-246, and PAPI were considered as substitutes.

Binders were prepared to evaluate GTRO as a crosslinking agent for Telagen binders. Two diisocyanates, hexamethylene diisocyanate (HDI) and DDI-1410 (dimeryl diisocyanate; General Mills) were used. Two diols, Polycin 23 and 51 from Baker Castor Oil Co., were also evaluated as co-diols. Since difficulty was encountered in obtaining consistent cures with a 1 to 1 NCO to OH ratio, a 1.05 ratio was used in most of the formulations.

The data in Table VI show that a significantly lower crosslink density is obtained with DDI-1410 than with HDI (compare Binders 218A with 219A, 224 with 225, 226 with 228, and 232 with 233). This results in higher elongations and lower moduli. These results were confirmed in propellant studies (Table IX). Compare Propellant 3837 with 3838 or 3835 with 3944.

Another interesting aspect of the use of GTRO is revealed in the data in Table X and the Figures 6 and 7 which show the relation between the uniaxial maximum (= break) tensile strength and initial modulus and crosslink density. The Binders 211 to 235 made with Prepolymer 148AH and GTRO do not have properties - crosslink relation shown by the Binders 239 to 254, all of which were crosslinked by isocyanates. The GTRO-crosslinked binders have almost no dependence upon crosslink density.

It is unlikely that this is due to Prepolymer 148AH because the properties of Prepolymer 3HPL-125 which is 93% saturated vary with the crosslink density and the properties of CTI-crosslinked binders of Prepolymer 148AH have been shown to be dependent upon the crosslink density of the binder (Figures 11 and 12, Report AFRL-TR-67-158). The effect may be related to the high NCO to OH ratio (1.05) used to cure these binders. Binders crosslinked with E-246 (No. 255) or PAPI (Nos. 257, 258 and 260) have properties which depend upon the crosslink density.

Table X

RELATION OF CROSSLINK DENSITY AND MECHANICAL BEHAVIOR
OF HYDROCARBON BINDERS

Ref. No.	Prepolymer	Crosslinker	Crosslink Density 10^5 moles chain/cc	Mechanical Properties at 77°F		
				σ_m psi	ϵ_m %	E psi
211	148AH	CTI	1.07	17	198	17
218A	148AH	GTR0	0.88	16	353	16
224	148AH	GTR0	0.67	17	452	10
225	148AH	GTR0	1.02	14	265	11
226	148AH	GTR0	1.87	17	226	20
235	148AH	GTR0	2.6	20	115	32
239	3HPL-90	CTI	0.14	7	716	8
239R	3HPL-90	CTI	0.32	18	712	17
240	3HPL-90	CTI	0.31	17	720	15
240R	3HPL-90	CTI	0.36	22	720	17
241	3HPL-90	CTI	0.22	13	711	14
241R	3HPL-90	CTI	0.41	23	713	19
242	3HPL-90	CTI	0.50	26	694	19
242R	3HPL-90	CTI	0.40	11	716	7
255	3HPL-90	E-246	0.30	10	523	13
257	3HPL-90	PAPI	0.21	10	719	9
258	3HPL-90	PAPI	0.05	2	711	6
260	3HPL-90	GTR0/PAPI	0.19	9	720	10
243	3HPL-125	CTI	0.15	6	705	10
244	3HPL-125	CTI	0.24	9	709	7
245	3HPL-125	CTI	0.23	8	706	6
246	3HPL-125	CTI	0.44	19	708	2
247	3HPL-123	CTI	0.13	5	707	2
248	3HPL-123	CTI	0.10	3	765	2
249	3HPL-123	CTI	0.26	10	705	3
250	3HPL-123	CTI	0.35	9	500	2
251	169	CTI	0.18	7	706	6
252	169	CTI	0.32	12	480	6
253	169	CTI	0.30	11	571	6
254	169	CTI	0.40	12	450	8

EFFECT OF CROSSLINK DENSITY ON BINDER TENSILE STRENGTH

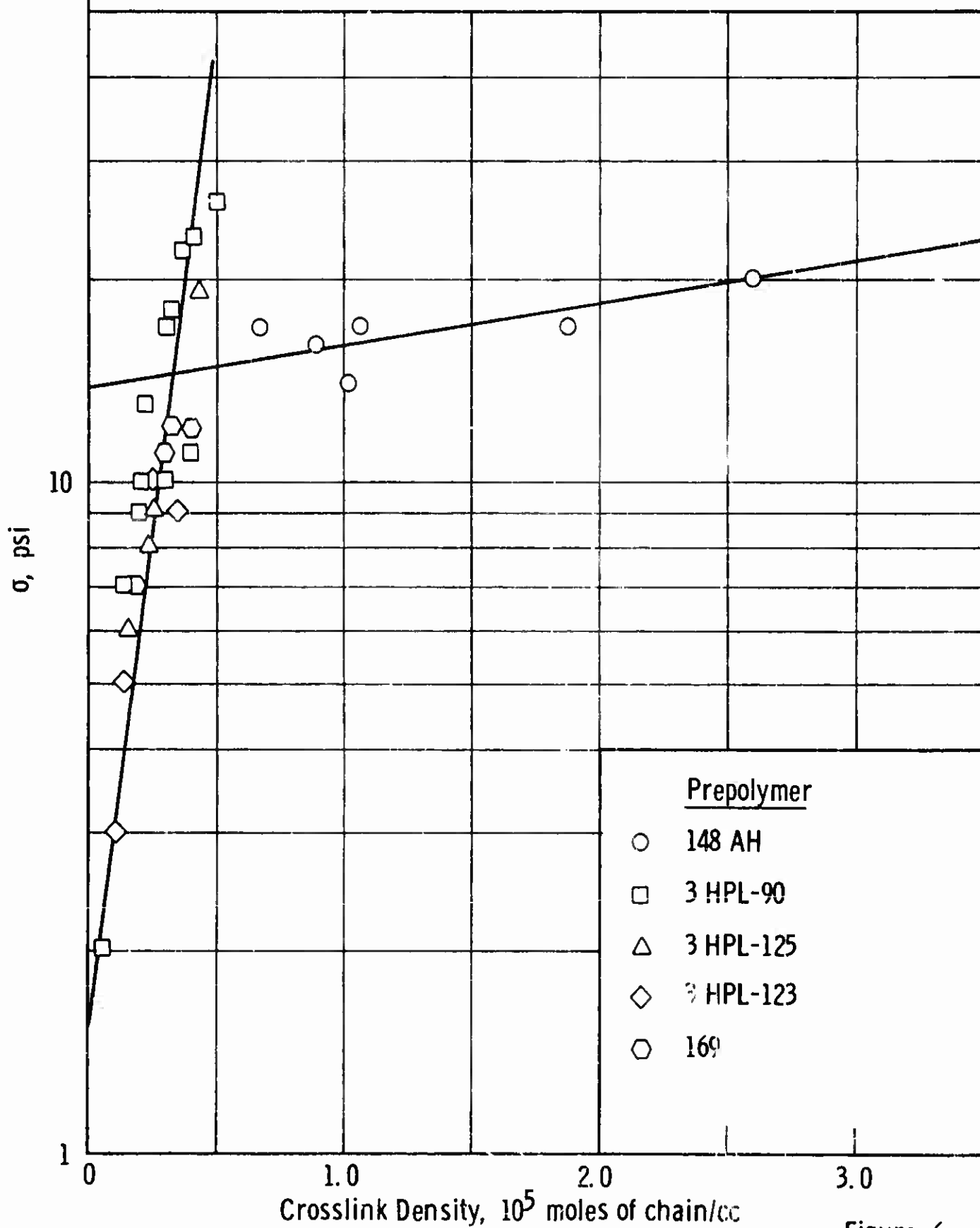


Figure 6

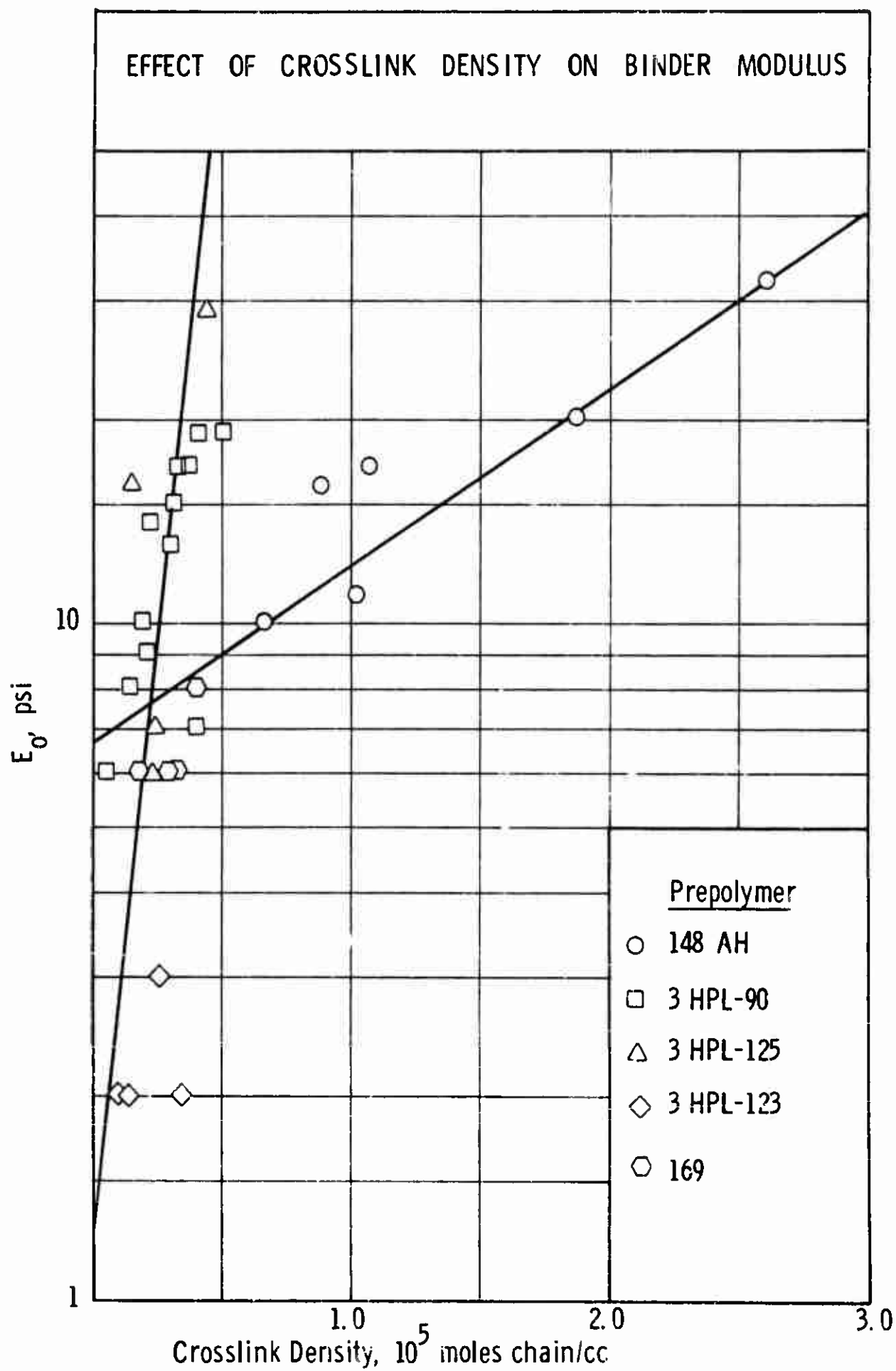


Figure 7

B. TASK TWO

1. Introduction

Task Two involves the determination of the compatibility of the prepolymers and curing agents with combinations of advanced oxidizer and advanced fuel. Model compounds are being used to study the binder component interactions with the fuels and oxidizers, and attempts are being made to improve systems which have poor compatibility. Compatible systems will be evaluated ballistically at the 1-lb scale.

2. Model Studies

a. Introduction

The compatibility and reactivity studies reported here were done with model compounds to simulate various functional characteristics of prepolymers and curing agents. These model compounds could be readily analyzed or identified by gas-liquid chromatography and by infrared analysis. In general these studies were made in benzene to simulate the non-polar nature of the hydrocarbon polymer chain and at concentrations typical for propellant system. An internal standard was included to calibrate the detector response.

b. 1-Acetylazetidine

The compatibility of 1-acetylazetidine in benzene with HAP and the reaction of the azetidine with propionic acid also in benzene in the presence of this oxidizer were studied. The gas chromatographic data indicated that acetylazetidine is not compatible with HAP. The azetidine disappeared from solution immediately. Since the solution of HAP neutralized with saturated aqueous potassium bicarbonate did not regenerate the azetidine in the benzene phase, the azetidine reacted with HAP rather than being adsorbed. After 2 days at 23°C and 50°C, there was no loss of propionic acid.

c. 2,5-Dioxaspiro[3,3]heptane

The compatibility of the oxetane, dioxaspiroheptane with HAP and HDP and its reaction with propionic acid in the presence of HAP and HDP were studied. Gas chromatographic data of the reactions are shown in Table X.

The oxetane showed poor compatibility with HAP but good stability in the presence of HDP. The reaction of the oxetane with propionic acid in the presence of HAP and HDP did not occur under the reaction conditions studied. A catalyst or change in the oxetane structure may promote the reaction between oxetane and acid in the presence of HDP. This work is not presently being pursued.

Table XI

EXTENT OF REACTION OF DIOXASPIROHEPTANE (1.75N) AND
PROPIONIC ACID (1.75N) IN THE PRESENCE OF
HAP AND HDP (80%) AFTER 18 HOURS IN BENZENE

<u>Oxidizer</u>	<u>Temp., °C</u>	<u>Amount Remaining, Wt.% of Original</u>	
		<u>Propionic Acid</u>	<u>Oxetane</u>
HAP	23	-	64
	23	100	40
	50	-	0
	50	97	0
HDP	23	-	90
	23	100	92
	50	-	82
	50	100	88

d. Reaction of Alcohols with Anhydrides in the
Presence of Advanced Oxidizers

The reaction of 2-octanol with n-1-decenylsuccinic anhydride in the presence of HAP and HDP did not follow the anticipated reaction path. Instead of the alcohol reacting with the anhydride, the alcohol was dehydrated to form 2-octene. The octene was isolated in a refrigerated multiple internal reflectance cell as it passed from the chromatograph (Figure 8), and identified from its infrared spectrum (Figure 9). The rate data in Table XII indicate that the alcohol was consumed and the alkene was formed at the same rate. Presumably, the anhydride loss was due to reaction with water formed from the dehydration of the alcohol. The dehydration of ethanol by HAP has been reported by workers at the Midwest Research Institute.⁽¹⁾

⁽¹⁾ A. D. McElroy and J. W. Nebgen, "Studies of Stability Problems in Advanced Propellants", Midwest Research Institute, Quarterly Progress Report No. 3, 1 April - 30 June 1967, 21 July 1967, Contract FO4611-67-C-0022 (Confidential).

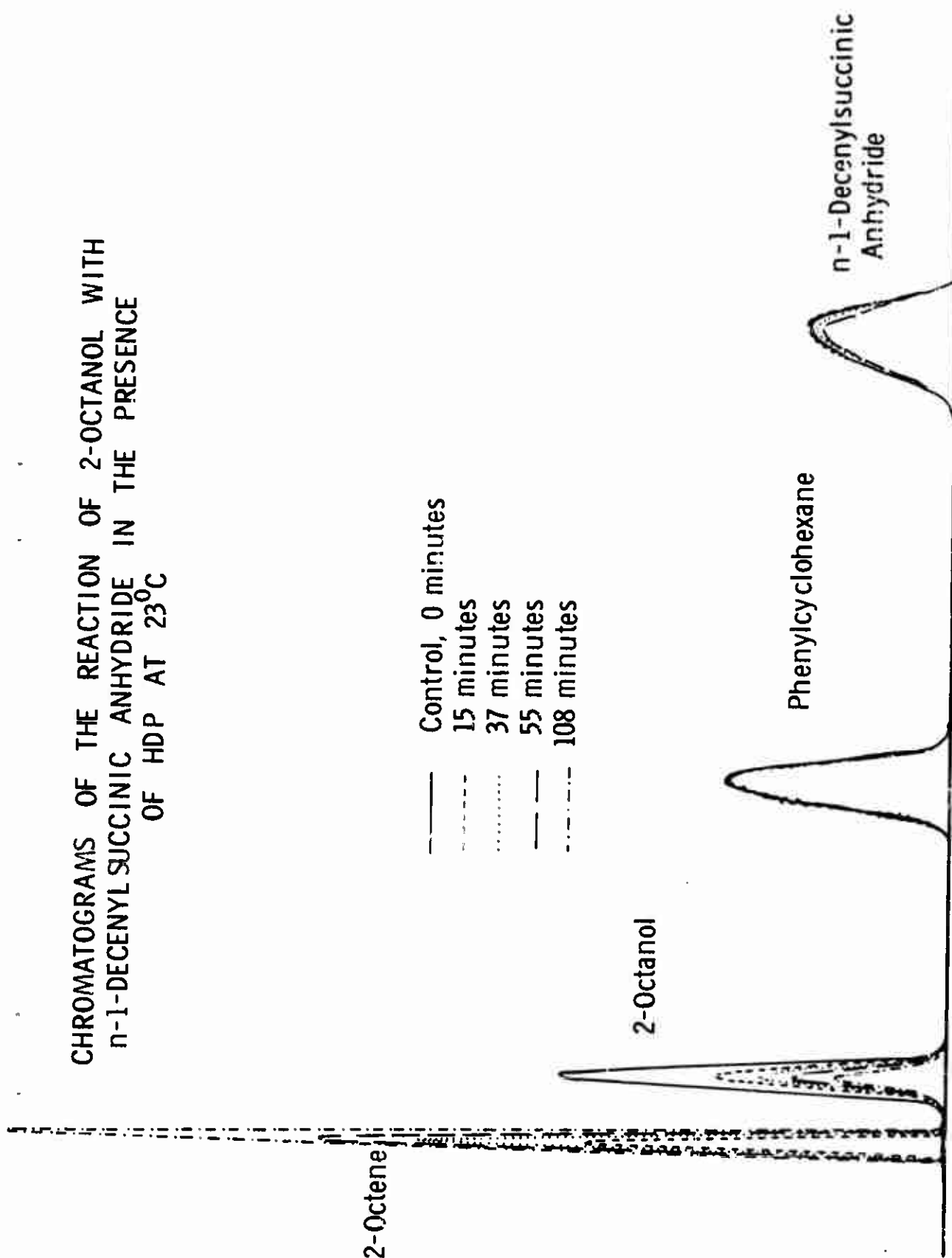
Table XII

REACTION OF 2-OCTANOL (0.88N) WITH n-1-DECENYLSUCCINIC
ANHYDRIDE (0.88N) IN THE PRESENCE OF HAP AND HDP (80%)
AT 23°C IN BENZENE

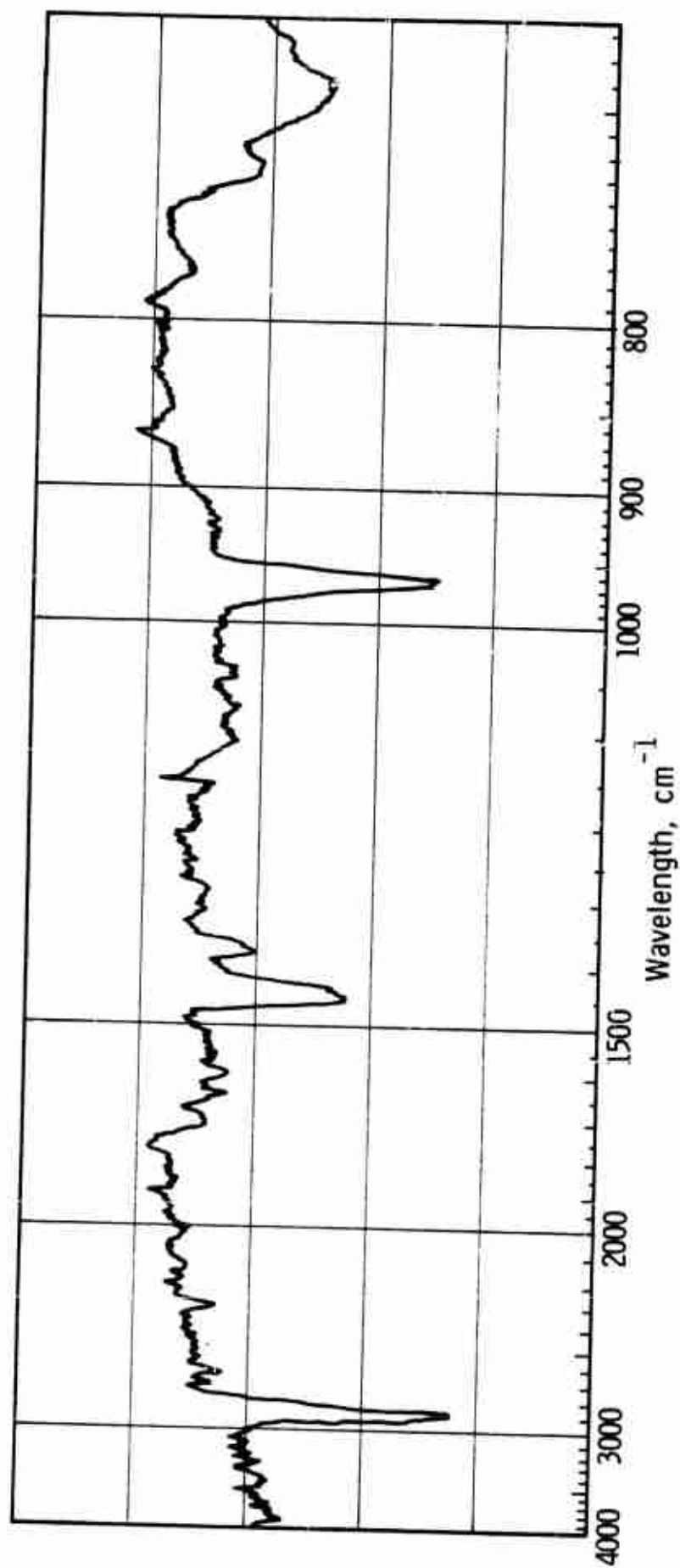
<u>Solid</u>	<u>Time, Minutes</u>	<u>Concentration, Wt.% Original</u>		
		<u>2-Octene^a</u>	<u>2-Octanol</u>	<u>Anhydride</u>
HDP	0	0	100	100
	15	42	50	77.5
	37	61	37	69
	55	67	32	62
	108	80	19	57
HAP	0	0	100	100
	10	12.5	85	88.5
	20	-	82	-
	30	24.4	74	86
	50	30.7	-	-
	90	41.8	60	67
	150	54.2	47.5	69

^a % of original octanol.

CHROMATOGRAMS OF THE REACTION OF 2-OCTANOL WITH
n-1-DECENYLSUCCINIC ANHYDRIDE IN THE PRESENCE
OF HDP AT 23°C

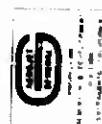


INFRARED SPECTRUM OF MATERIAL ISOLATED BY GLC
(Compare with 2-Octane, Sadtler Standard Spectra 16155)



-36-
Transmittance, %

Figure 9



A weak base, ethyl N-phenylcarbamate (1 to 1 equivalents ratio to HDP), was added to the reaction solution to decrease the acidic nature of HDP. The data in Table XIII show that addition of the carbamate had no effect on the reaction. That the carbamate was neither adsorbed by nor reacted with HDP was demonstrated by the following. A sample of HDP was titrated with 0.1N KOH in methanol to a phenolphthalein end point. The titration values for three samples made up in molar ratios of 0.5, 1.0, and 1.5 ethyl N-phenylcarbamate to HDP were the same as that of the control without carbamate indicating that no reaction or adsorption had taken place. This point was further demonstrated by the fact that, as indicated by gas chromatography, the ethyl N-phenylcarbamate concentration did not change as the reaction progressed between decenylsuccinic anhydride and octanol in the presence of HDP.

Table XIII

REACTION OF 2-OCTANOL (0.88N) WITH n-1-DECENYLSUCCINIC ANHYDRIDE (0.88N) IN THE PRESENCE OF HDP (80%) AT 23°C AND ETHYL N-PHENYLCARBAMATE IN BENZENE

Time, Minutes	Concentration, Wt.% of Original			
	<u>2-Octene^a</u>	<u>2-Octanol</u>	<u>Carbamate</u>	<u>Anhydride</u>
10	47.5	54	97	85.5
30	49	50	96	88.5
90	68.5	26.7	87	77.0
135	84.4	17.8	94	-

^a % of original octanol.

On the other hand, the reaction of 1-octanol with n-1-decenyl-succinic anhydride apparently gave the expected ester but at too rapid a rate to be of use as a propellant cure system (Table XIV). The octanol was consumed somewhat more rapidly than the anhydride. This was not due to dehydration, because the octene peak was not observed on the chromatogram. A possible reaction is that of octanol with the acid group of an anhydride which has already undergone ring opening.

Table XIV

REACTION OF 1-OCTANOL (0.88N) WITH n-1-DECENYLSUCCINIC
ANHYDRIDE (0.88N) IN THE PRESENCE OF HDP (80%)
AT 23°C IN BENZENE

<u>Time</u> <u>Minutes,</u>	<u>Amount Remaining,</u> <u>Wt.% of Original</u>	
	<u>1-Octanol</u>	<u>Anhydride</u>
15	34.6	54.2
35	20.7	40.4
60	15.8	34.6
120	9.2	33.2

2-Ethylhexanol was substituted for 1-octanol to slow the rate of the anhydride alcohol reaction. The rate increased instead of decreasing (Table XV). A change of the anhydride from n-1-decenyl (unsaturated) to dodecylsuccinic slowed the rate to that observed with 1-octanol indicating that the conjugated double bond increases the reactivity of the anhydride (Table XVI).

Table XV

REACTION OF 2-ETHYLHEXANOL (0.88N) WITH n-1-DECENYLSUCCINIC
ANHYDRIDE (0.88N) IN THE PRESENCE OF HDP (80%)
AT 23°C IN BENZENE

<u>Time,</u> <u>Minutes</u>	<u>Compound Remaining</u> <u>Wt.% of Original</u>	
	<u>2-Ethylhexanol</u>	<u>Anhydride</u>
10	26	40
30	8.9	27.8
60	8.3	26.4

Table XVI

REACTION OF 2-ETHYLHEXANOL (0.88N) WITH n-DODECYLSUCCINIC
ANHYDRIDE (0.88N) IN THE PRESENCE OF HDP (80%)
AT 23°C IN BENZENE

<u>Time, Minutes</u>	<u>Compound Remaining, Wt.% of Original</u>	
	<u>Alcohol</u>	<u>Anhydride</u>
15	40.3	42.6
40	22.2	22.4
90	15.2	18.6

Repeat experiments (Tables XVII and XVIII) indicated that the reactions were too rapid to establish accurately which reaction was faster. The reaction of 1-octanol with dodecylsuccinic anhydride was studied to compare it with the reaction of 1-octanol with the corresponding unsaturated compound, n-1-decenylsuccinic anhydride. The data in Table XIX compared with previous data indicate that these reactions were also too rapid to establish accurately which reaction was faster.

Table XVII

REACTION OF 1-OCTANOL (0.88N) WITH n-1-DECENYLSUCCINIC
ANHYDRIDE (0.88N) IN THE PRESENCE OF HDP (80%)
AT 23°C IN BENZENE

<u>Time, Minutes</u>	<u>Compound Remaining, Wt.% of Original</u>	
	<u>1-Octanol</u>	<u>Anhydride</u>
2	21.2	31.5
20	-	28.2
45	14.9	25.4
60	14.7	20.6

Table XVIII

REACTION OF 2-ETHYLHEXANOL (0.88N) WITH n-1-DECENYLSUCCINIC
ANHYDRIDE (0.88N) IN THE PRESENCE OF HDP (80%)
AT 23°C IN BENZENE

<u>Time, Minutes</u>	<u>Compound Remaining, Wt.% of Original</u>	
	<u>Alcohol</u>	<u>Anhydride</u>
2	27.0	42.7
20	13.2	32.6
45	-	25.2
60	9.3	21.7
90	8.9	24.4

Table XIX

REACTION OF 1-OCTANOL (0.88N) WITH DODECYLSUCCINIC
ANHYDRIDE (0.88N) IN THE PRESENCE OF HDP (80%)
AT 23°C IN BENZENE

<u>Time, Minutes</u>	<u>Compound Remaining, Wt.% of Original</u>	
	<u>1-Octanol</u>	<u>Anhydride</u>
2	28.2	30.4
25	17.1	20.5
120	14.0	18.5

Further studies on the dehydration of 2-octanol to 2-octene in benzene solution and in the presence of HDP, indicated that a stirred solution gave complete dehydration after 30 seconds of reaction at room temperature. A similar test with HAP indicated a 4 percent conversion to alkene after 30 seconds. In view of these facts, further propellant formulations for the advanced oxidizers will utilize other approaches;

including the use of alcohols and prepolymers terminated with primary hydroxyl groups rather than secondary hydroxyl groups to minimize the dehydration side reaction and loss of functionality. The observation of the dehydration reaction is significant for the future development of isocyanate cured HDP or HAP propellants.

3. HAP Propellants

A one-pound batch of HAP propellant was made using the isocyanate, Carwinate 125M, in an effort to improve mechanical properties. The propellant became firm, but very little, if any, crosslinking occurred. There were no signs of incompatibility or HAP degradation. The oxidizer used for the batch was impure HAP which had been recrystallized, but was probably still not as pure or as dry as it could have been.

The recrystallized HAP was further purified by a process used to make spheroidal particles. Two 50-gram batches were made with the spheroidal HAP at different crosslink levels using Carwinate 125M. These batches cured in three days. The extent of cure was not as complete as has been previously obtained using HAP which was known to be pure.

Ten gram propellant batches were made using prepolymer with primary hydroxyl groups. Two HAP propellants were made using primary hydroxyl prepolymer (168H), TMP and Carwinate 125M. One was plasticized with IDP; the other, with Oronite 6. Each of these batches was divided in half. One-half was cured at 40°C and the other, at 70°C.

Samples cured at high temperature turned green and gelled within four hours. The samples cured at the lower temperature gelled overnight. The low temperature IDP sample had turned green but the Oronite 6 sample remained at the original grey color. None of these propellants was satisfactory, but the Oronite 6 sample which was cured at low temperature (40°C) was the best.

Another series of three 10-gram HAP propellants was made using Oronite 6 and a 40°C cure temperature. Both Carwinate 125M and TMP which are solid at room temperature and insoluble in the prepolymer, were finely ground by a mortar and pestle prior to dispensing.

The first two batches were made with Prepolymer 168H, TMP (80 to 20 equivalents ratio of 168H to TMP), and Carwinate 125M and the third was made with GTRO in place of TMP (prepolymer to GTRO ratio, 60/40). The TMP-crosslinked batches became very hard but showed little evidence of crosslinking. The third batch with 60 to 40 equivalents ratio of 168H to GTRO was well cured overnight and showed good resilience. This propellant was the best of this series.

A portion of each of the three propellants was catalyzed with $\text{TiO}(\text{AA})_2$, but there was no difference between the catalyzed and uncatalyzed portions.

4. HLP Propellant

A 10-gram batch of HDP propellant was made using hydroxy terminated prepolymer, GTR0 and Carwinate 125M. This propellant cured within an hour. The following safety data was obtained.

Bureau of Mines Impact (50% PT), cm/2kg	1.0g
Friction Sensitivity (50% PT), 1000 gm load 5200 rpm	
DTA - Onset of exotherm, °F	223
Exotherm peaks, °F	324, 335, 348
Endotherm peak, °F	193

The systematic study of the chemistry of HAP and HDP propellants will be continued and improvements will be introduced until a satisfactory advanced propellant has been formulated and tested.

C. TASK THREE

1. Introduction

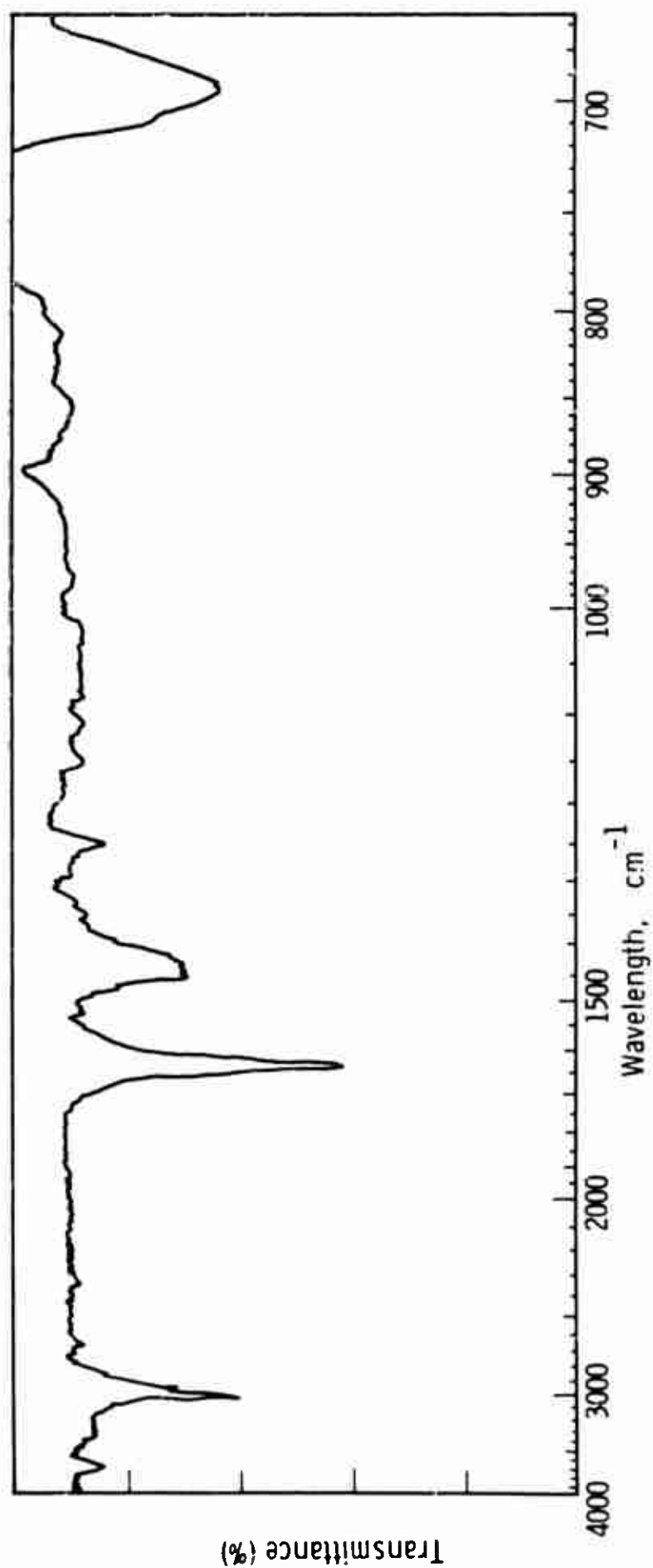
The achievement of a room temperature cure and obtaining a suitable replacement for CTI are the main studies for Task Three. The synthesis of curing agents on an "as needed" basis is also being performed.

2. Preparation of 1-Acetylazetidine

Into a 2-neck, 100-ml round-bottom flask fitted with a dropping funnel, thermometer and magnetic stirrer and containing 30 ml of water and 20 ml of methylene chloride were placed 2.6 grams of potassium carbonate and 1.07 grams (0.019 moles) of acetyl chloride in 10 ml of methylene chloride was added through a dropping funnel at a rate to maintain the temperature between 0 and 5°C. The reaction was stirred at 0°C for one-half hour after completion of the addition.

The two phases of the reaction solution were separated. The methylene chloride phase was washed twice with 10 ml of 2N aqueous sodium hydroxide and then dried over 3 grams of sodium sulfate. After removal of the methylene chloride, the crude yield was 0.53 grams (27%). The material was of greater than 95% purity by gas chromatography. Identification was made by infrared spectrum, Figure 10.

INFRARED SPECTRUM OF 1-ACETYLAZETIDINE IN
METHYLENE CHLORIDE



-13-
Transmittance (%)

Figure 10



. D. TASK FOUR

1. Introduction

Task Four includes Phase Four (propellants in aging before March 1967) and also involves the aging of propellants prepared under Tasks One and Two. It further includes the testing at 350°C of selected Task One propellants and the temperature cycling of propellants made with a CTI replacement.

2. Effect of Prepolymer Saturation on Binder Aging

Aging studies have been initiated to determine the effect of oxidative crosslinking on binders prepared from prepolymers with various degrees of unsaturation. The samples are being aged at 80°C in a circulating air atmosphere. The control samples are being aged in the same oven but are sealed in ampules having an argon atmosphere. The samples will be studied by a micro-swelling technique to determine the extent of oxidative effects. No data are available for this report.

3. Aging of Conventional Propellants

In Tables XX to XXVIII, the aging data are presented for conventional Telagen S propellants and Minuteman propellant stored as long as 9 months. The new data do not alter the basic pattern. This pattern is a pronounced deterioration caused by moisture especially at higher temperature. The unsaturated Minuteman propellant also shows oxidative crosslinking which eventually increases the propellant modulus. The aging is continuing.

Table XX

MECHANICAL BEHAVIOR OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT -75°F AND 100% RELATIVE HUMIDITY IN CARBON DIOXIDE ENVIRONMENT

Time in Aging Weeks	Mechanical Properties at 77°F, $\sigma_u/\sigma_b/\epsilon_u/\epsilon_b/E$			
	Telagen S		Minuteman	
	66-954	67-98	67-260	
	Samples Unwrapped			
0	100/93/24/28/650	123/-/35/45/605	58/54/45/57/205	135/133/16/19/1250 ^b
1	-	129/123/39/42/770	79/77/41/48/365	-
2	111/96/21/30/826	141/136/35/43/743	78/74/42/53/356	135/133/16/19/1330
4	115/100/24/33/754	132/123/33/44/756	70/68/43/50/29	136/130/16/22/1306
9	111/100/23/30/843	-	72/70/40/44/295	128/124/17/21/1160
26	114/96/22/32/850	-	-	126/122/18/25/1045
39	-	122/116/27/36/835	-	-
	Samples Al Foil Wrapped			
0	100/93/24/28/650	123/-/35/45/605	58/54/45/57/205	135/133/16/19/1250 ^b
1	-	131/124/31/42/770	78/75/42/50/365	-
2	114/96/22/32/843	132/126/31/40/952	75/72/42/50/363	124/123/18/20/1009
4	115/94/21/32/856	130/123/33/44/712	76/72/41/51/354	134/130/17/22/1173
9	105/92/21/30/802	-	68/65/43/50/289	121/119/19/24/950
26	97/84/21/30/717	-	-	123/112/20/25/925
39	-	135/131/30/39/835	-	128/125/15/19/1278

^aPropellants all contain 98 wt% solids.

^bThese values are values after aging at room temperature before storage begun.
properties after 12 day cure 90/-/34/45/125.

Table XXI

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT 0°F AND 100% RELATIVE HUMIDITY IN CARBON DIOXIDE ENVIRONMENT

Time in Aging Weeks	Mechanical Properties at 77°F, $\sigma_s/\sigma_u/\sigma_c/\sigma_t/\sigma_e/\sigma_b/E$				
	Telagen S		Minuteman		
	66-954	67-98	67-260		
	Samples Unwrapped				
0	100/93/24/28/650	123/-/34/45/605	58/54/45/57/205	135/133/16/19/1250 ^b	
1	112/108/21/26/808	129/124/34/43/672	80/78/41/46/363	135/133/16/19/1256	
2	107/100/18/23/800	143/136/33/42/789	76/73/42/50/341	113/112/14/20/1130	
4	110/103/21/28/800	131/124/35/43/682	73/70/42/50/321	131/129/17/20/1167	
9	118/110/22/30/859	-	73/71/42/50/313	134/132/16/19/1265	
26	100/82/22/34/765	118/111/29/37/721	-	136/118/16/23/1325	
39	-	-	-	129/120/15/20/1420	
Samples Al Foil Wrapped					
0	100/93/24/28/650	123/-/35/45/605	58/54/45/57/205	135/133/16/19/1250 ^b	
1	114/108/22/28/865	136/131/33/40/759	76/73/38/46/337	136/133/17/21/1167	
2	108/102/21/28/780	142/137/36/43/730	80/77/42/50/350	135/132/18/22/1110	
4	106/100/21/27/817	135/128/34/43/723	76/72/43/52/330	116/113/20/24/850	
9	104/96/21/27/789	-	74/71/43/53/300	133/130/18/21/1158	
26	112/96/22/32/818	102/94/27/39/671	-	132/118/17/22/1105	
39	-	-	-		

^a Propellants all contain 88 wt% solids.

^b These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XXII

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT 77°F AND 5% RELATIVE HUMIDITY IN STAGNANT ARGON ENVIRONMENT

Time in Aging Weeks	Mechanical Properties at 77°F, $\sigma_e/\alpha_e/\epsilon_e/\epsilon_h/E$				
	Telagen S				
	66-954	67-98	Samples Unwrapped		
0	100/93/24/28/650	123/-/35/45/605	58/54/45/57/205	135/133/16/19/1250 ^b	
1	114/99/21/30/915	128/126/33/38/704	75/73/42/50/328	138/135/16/19/1159	
2	116/100/22/31/894	126/117/32/44/795	77/74/41/51/343	136/134/17/20/1156	
4	112/101/21/29/861	134/137/34/43/743	73/71/42/49/313	146/144/16/20/1374	
9	111/104/21/32/824	-	76/75/44/49/346	134/130/18/22/1112	
26	115/98/22/32/843	-	-	141/133/18/22/1920	
39	110/104/22/28/819	112/103/28/39/776	-	153/149/15/18/1666	
Samples Al Foil Wrapped					
0	100/93/24/28/650	123/-/35/45/605	58/54/45/57/205	135/133/16/19/1250 ^b	
1	118/100/22/32/852	129/124/33/40/732	73/71/40/46/315	129/128/19/19/1114	
2	109/106/19/24/784	124/121/27/33/688	77/74/41/51/356	136/134/15/18/1374	
4	111/94/22/31/808	126/121/33/42/686	74/73/40/44/332	141/139/17/19/1225	
9	112/107/21/30/824	-	76/74/43/50/335	127/125/16/19/1105	
26	116/100/21/31/836	98/80/25/41/697	-	135/126/19/22/1120	
39	114/107/22/28/843	114/103/26/38/848	-	143/138/14/18/1671	

^aPropellants all contain 88 wt% solids.

^bThese values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XXIII

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTENAN WING VI SECOND STAGE PROPELLANTS^a
AT 77°F AND 50% RELATIVE HUMIDITY IN STAGNANT ARGON ENVIRONMENT

Time in Aging Weeks	Mechanical Properties at 77°F, $\sigma_s/\sigma_b/\epsilon_s/\epsilon_b/E$				
	Telagen S				
	66-954	67-98	67-260	Minuteman	
	Samples Unwrapped				
0	100/93/24/28/650	123/-/35/45/605	58/54/45/57/205	135/133/19/19/1250 ^b	
1	115/96/22/31/808	133/125/35/43/699	77/75/42/47/337	128/124/18/22/1101	
2	117/96/21/32/883	123/115/32/44/721	77/72/44/54/354	143/131/15/22/1549	
4	113/96/22/32/787	129/122/32/42/763	74/71/42/49/319	138/127/17/23/1254	
9	103/98/20/30/749	-	77/73/43/52/341	115/111/20/26/843	
26	108/100/20/26/911	-	-	142/131/15/19/1565	
39	-	-	-	130/127/19/23/1193	
	</				

^aPropellants all contain 88 wt% solids.

^bThese values are values after aging at room temperature before storage begun.
Properties after 12 day cure 90/-/34/45/425.

Table XXIV

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT 77°F AND 25% RELATIVE HUMIDITY IN CIRCULATING AIR ENVIRONMENT

Time in Aging Weeks	Mechanical Properties at 77°F, $\sigma_b/\sigma_0/\epsilon_b/\epsilon_0/E$				
	Telagen S		Minuteman		
	66-954	67-98	67-260	Unwrapped	
0	100/93/24/28/650	123/-/35/115/605	58/54/45/57/205	135/133/16/19/1250 ^b	
1	118/99/21/30/933	130/124/33/112/7143	74/70/43/53/326	124/121/19/23/1057	
2	118/100/23/33/789	127/119/32/113/839	75/71/39/50/350	110/137/19/22/1160	
4	115/99/22/32/900	132/124/33/114/758	75/70/43/54/330	146/144/16/19/1402	
9	124/118/23/30/867	-	78/75/39/45/380	126/125/17/20/1099	
26	90/73/18/29/711	124/117/32/112/792	-	122/108/19/26/1095	
39	129/123/23/30/972	-	-	113/171/12/11/2610	
Samples Al Foil Wrapped					
0	100/93/24/28/650	123/-/35/115/605	58/54/45/57/205	135/133/16/19/1250 ^b	
1	116/100/22/32/804	128/122/34/112/683	80/78/43/48/348	138/136/17/20/1250	
2	116/104/23/30/778	126/119/33/113/758	79/77/43/50/343	126/124/22/25/983	
4	115/96/22/32/856	129/121/33/114/756	73/70/43/50/315	216/113/16/20/1439	
9	112/108/21/30/850	-	76/74/42/50/339	119/115/20/23/922	
26	89/71/20/29/891	130/123/32/110/863	-	139/126/16/21/1360	
39	124/117/23/30/946	-	-	152/151/11/17/1632	

^aPropellants all contain 8% wt% solids.

^bThese values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/71/115/115.

Table XXV

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT 77°F AND 50% RELATIVE HUMIDITY IN CIRCULATING AIR ENVIRONMENT

Time in Aging Weeks	Mechanical Properties at 77°F, $\sigma_t/\sigma_0/\epsilon_t/\epsilon_0/E$			
	Telagen S		Minuteman	
	66-954	67-98	67-260	Minuteman
		Samples Unwrapped		
0	100/93/24/28/650	123/-/35/45/605	58/54/45/57/205	135/133/16/19/1250 ^b
1	116/100/22/30/870	131/124/33/41/737	76/72/41/50/367	140/136/16/20/1413
2	-	121/115/32/42/758	74/70/43/55/315	136/133/18/20/1232
4	-	125/119/33/43/671	71/68/44/52/324	112/108/19/26/870
9	-	-	75/74/44/51/350	116/113/19/22/1020
26	-	100/83/26/42/651	-	143/131/17/22/1840
39	-	109/93/26/42/752	-	149/148/14/15/1747
		Samples Al Foil Wrapped		
0	100/93/24/28/650	123/-/35/45/605	58/54/45/57/205	135/133/16/19/1250 ^b
1	112/98/21/30/878	124/114/31/43/759	76/73/40/47/356	142/140/17/20/1234
2	-	124/116/32/43/719	75/72/44/52/330	133/130/18/21/1162
4	-	127/118/32/44/725	75/73/41/47/326	132/129/16/24/1143
9	-	-	75/72/40/48/253	133/130/16/19/1241
26	-	-	-	139/125/16/22/1175
39	-	109/100/27/37/701	-	137/133/16/19/1398

^a Propellants all contain 88 wt% solids.

^b These values are values after aging at room temperature before storage begun.
Properties after 12 day cure 90/-/34/45/425.

Table XXVI

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT 77°F AND 80% RELATIVE HUMIDITY IN STAGNANT AIR ENVIRONMENT

Time in Aging Weeks	Mechanical Properties at 77°F, $\sigma_c/\sigma_b/\epsilon_c/\epsilon_b/E$				
	Telagen S			Minuteman	
	66-954	67-98	67-260		
	Samples Unwrapped				
0	100/93/24/28/650	123/-/35/45/605	58/54/45/57/205	135/133/16/19/1250 ^b	
1	108/96/20/27/841	130/124/32/41/754	75/73/40/46/352	137/135/16/18/1280	
2	107/92/21/30/776	118/104/31/45/677	74/73/42/48/356	143/141/15/19/1501	
4	96/75/21/31/688	120/110/32/44/664	73/70/42/70/330	134/121/16/24/1350	
9	60/50/22/35/439	-	61/57/39/51/276	115/115/15/22/1025	
26	40/38/24/33/317	42/48/31/59/362	-	104/91/15/20/935	
39	-	-	-	-	
Samples Al Foil Wrapped					
0	100/93/24/28/650	123/-/35/45/605	58/54/45/57/205	135/133/16/19/1250 ^b	
1	115/94/22/32/804	129/123/32/40/759	77/75/42/47/343	145/143/16/19/1350	
2	109/90/22/32/787	120/104/33/47/649	74/73/43/47/339	138/136/17/20/1195	
4	94/76/22/32/594	121/110/30/43/730	74/70/43/55/335	128/116/16/23/1243	
9	67/57/22/34/468	-	63/58/39/53/297	112/109/16/23/931	
26	23/13/29/90/180	59/45/26/47/485	-	100/91/16/19/865	
39	-	-	-	104/94/18/25/819	

^a Propellants all contain 88 wt% solids.

^b These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XXVII

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT 170°F AND 25% RELATIVE HUMIDITY IN CIRCULATING AIR ENVIRONMENT

Time in Aging Weeks	Mechanical Properties at 77°F, $\alpha_s/\alpha_0/e_s/e_0/E$				
	Telagen S				
	66-954	67-98	67-260		Minuteman
			Samples Unwrapped		
0	100/93/24/28/650	123/-/35/45/605	58/54/45/57/205	135/133/16/19/1250 ^b	
1	85/82/26/30/507	86/77/34/46/439	50/44/42/57/295	124/117/31/45/756	
2	65/64/25/28/394	45/20/28/68/477	43/36/45/67/280	111/110/33/38/653	
4	40/39/22/25/252	103/98/33/41/560	20/19/40/46/175	78/77/24/26/608	
9	47/47/19/22/367	-	32/16/23/30/374	71/67/11/16/990	
26	-	-	-	79/78/10/12/1502	
39	-	-	-	-	
			Samples Al Foil Wrapped		
0	100/93/24/28/650	123/-/35/45/605	58/54/45/57/205	135/133/15/19/1250 ^b	
1	95/88/28/36/494	94/84/32/44/514	63/58/40/52/280	107/101/33/44/507	
2	62/61/26/29/352	46/24/30/71/396	48/40/45/67/242	105/98/31/46/555	
4	43/42/25/28/263	100/89/37/53/461	32/24/52/81/184	66/66/11/12/780	
9	46/45/24/28/293	-	52/45/49/70/241	100/99/6/6/2200	
26	66/65/21/23/520	-	-	-	
39	-	43/37/44/60/276	-	-	

^a Propellants all contain 88 wt% solids.

^b These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XXVIII

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
 AT 170°F AND 80% RELATIVE HUMIDITY IN STAGNANT AIR ENVIRONMENT

Time in Aging Weeks	Mechanical Properties at 77°F, $\sigma_s/\sigma_b/\epsilon_s/\epsilon_b/E$				
	Telagen S				Minuteman
	66-954	67-98	67-260		
	Samples Unwrapped				
0	100/93/24/28/650	123/-/35/45/605	58/54/45/57/205	135/133/16/19/1250 ^b	
1	48/18/21/21/289	54/51/31/38/343	30/21/46/71/206	104/90/24/39/577	
2	21/20/26/28/102	27/21/30/41/214	18/17/33/39/136	-	
4	22/22/27/30/97	30/28/24/28/195	12/12/30/33/63	-	
9	25/24/22/25/136	-	12/11/23/27/65	41/40/4/4/920	
26	14/9/26/36/88	-	-	30/30/3/3/920	
39	-	20/19/15/16/180	-	89/86/3/4/3183	
Samples Al Foil Wrapped					
0	100/93/24/28/650	123/-/35/45/605	58/54/45/57/205	135/133/16/19/1250 ^b	
1	69/66/27/32/365	56/48/34/48/323	41/30/44/71/254	120/110/27/42/699	
2	52/50/26/30/302	35/23/32/56/311	30/24/48/24/192	93/87/32/46/113	
4	36/35/25/28/196	48/47/30/34/294	25/20/43/53/186	70/69/18/19/570	
9	29/28/23/26/175	-	21/20/36/42/142	43/43/6/6/822	
26	20/13/25/43/136	-	-	-	
39	-	44/42/22/25/328	-	63/63/3/3/3500	

^a Propellants all contain 88 wt% solids.

^b These values are values after aging at room temperature before storage begun.

Properties after 12 day cure 90/-/34/15/425.

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13. ABSTRACT Air Force Systems Command United States Air Force <p>Work was continued on the study of Telagen S prepolymers for conventional and advanced propellant systems. The factors affecting low temperature behavior of conventional systems and a replacement for CTI received most attention this quarter. Saturation of Telagen prepolymers definitely causes poor low temperature properties in binders and propellants. This was established by studies with a series of related polymers differing only in saturation. Mixtures of saturated and unsaturated prepolymers were not as good as a partially saturated prepolymer for low temperature behavior. Prepolymer molecular weight and the nature of the crosslinker had very little effect on the low temperature mechanical properties. Telagen S prepolymers have been simplified and an infrared method was used to follow the functionality of the eluted polymer. Preparative chromatography to obtain difunctional prepolymer for binder and propellant studies was developed. Aging studies were continued and aging of binders with partially saturated prepolymers was begun.</p> <p>The study of advanced systems was continued by model compound and propellant investigations using HDP and HAP. Acetylazetidine and 2,5-dioxaspiro[3,3]heptane were incompatible with HAP and only the latter was compatible with HDP. However the dioxaspiroheptane did not react with acid at 50°C. It was observed that HAP and HDP very rapidly dehydrate secondary alcohols. With these materials only primary alcohols may be used. Some HAP propellants were made.</p>		

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